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QUALITY CONTROL PRACTICES IN PROCESSING AIR POLLUTION SAMPLES

PEDCo-Environmental Specialists, Incorporated

Prepared for
Environmental Protection Agency

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16. Abstracts The importance of a quality control program to assess and document the reliability of data is presented. The objective of this document is to provide guidance or instructions for agency personnel to assist in the development or modification of quality control programs. The major elements of the quality control program can be considered in two categories: control of the physical parameters and analysis of the total measurement process. The parameters are enumerated for atmospheric sampling, source sampling and the analytical laboratory and the appropriate quality control methods are described. Control of physical parameters is designed to reduce the frequency of occurance of errors in laboratory operation and procedures analysis is applied to determine the effectiveness of the physical control parameters. This can be determined by a number of statistical and other techniques. Problems associated with designing a program to monitor the analyst's performance is presented with suggested solutions. Analytical variability and techniques for control are presented. Additional topics presented are: documentation and demonstration of quality control; data recording; data validation; statistical approach to data validation; and interlaboratory proficiency testing. The information appended to this report is as follows: statistical formulas and control charts and calibration curves from regression analysis by the method of least squares.

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1.0 INTRODUCTION

1.1 General Considerations

State, regional and local air pollution control laboratories perform an array of technical services involving sample collection, sample analysis and data validation. To demonstrate that reliable data are reported, the technical services group must establish a quality control program. We define a quality control program as:

> ". . . THE PROGRAM APPLIED TO ROUTINIZED SYSTEMS (I.E., SYSTEMS COMPOSED OF METHODS, EQUIPMENT AND PEOPLE) IN ORDER TO EVALUATE AND DOCUMENT THE ABILITY OF A FUNCTION, ACTIVITY, OR PERSON TO PRODUCE RESULTS WHICH ARE VALID WITHIN PREDETERMINED ACCEPTANCE LIMITS".

It must be emphasized that we are speaking of "quality control" not "quality assurance", which we consider as encompassing both quality control and methods standardization. Further, quality control programs should be successfully implemented prior to involvement of a technical services group in cooperative-laboratory standardization efforts.

A quality control program is developed to minimize sources of variation inherent in all analytical and technical functions. Through the use of standard operating procedures and statistical techniques, items such as determinate errors are identified and controlled. The effects of random errors are measured and used to express the degree of confidence to be placed in the analytical data and to determine when the process that generates the data is not functioning properly.

The quality control program should be designed so that the supervisor, through his technicians, can set up a protocol for performing each operation involved in sample collection, analysis, and data handling. Implementation of the quality control program requires that descriptions of each procedure be readily available to the laboratory staff. This document is intended to provide the administrator or supervisor with guidelines for establishing a detailed quality control program that is consistent with his specific needs and objectives.

1.2 Importance of Quality Control

The functions of a technical services group in an air pollution control program encompass both field and laboratory operations, including surveillance of pollution sources, acquisition of ambient air quality data, episode criteria monitoring and performance of special studies. The technical services group provides qualitative and quantitative data to be used at all levels of program operation. Consequently, each sample procured must be adequately representative of emissions from the pollutant source or of the atmosphere sampled. In addition, analysis of the sample, performed in the field or in the laboratory, by automatic instrumentation or by wet chemical means, must provide data that accurately describe the qualitative or quantitative characteristics of the sample. In some instances, incorrect data could lead to faulty interpretations, and this could be worse than no data at all.

Important and far-reaching decisions may be based on air quality and emission data which sometimes may be presented as evidence in courts of law. Aerometric data will be used to determine whether standards are being met. If results indicate violation of a regulation, the appropriate enforcement group is required to take action. With the current emphasis on legal action and social pressures to abate pollution, personnel in the technical services group must be made aware of their responsibility to provide results that present a reliable description of the sample. In addition, the analyst should know that his professional competence, the procedures he uses, and the values he reports may be presented and challenged in court. To meet such a challenge, all data must be supported by a detailed program that documents the proper control of all factors affecting the reported result.

In testing of pollutant sources, the economic implications alone are sufficient reason for exercising extreme care in sampling and analysis. Plant operators may use these data as a basis for decisions to change a process, install control devices, or even to construct new facilities.

Special projects and short-range development studies in air pollution control must be based on sound laboratory data. The value of a development effort will depend on the validity of laboratory results. The progress of a special study and alternative experimental pathways, especially, are evaluated on the basis of accumulated data; the final results and recommendations are usually evaluated by presentation of data such as averages, standard deviations, ranges, frequency distribution, and confidence limits.

For these reasons and many more, a quality control program to assess and document the reliability of data is essential. Although most chemists, engineers, and technicians practice some personal form of quality control, they do so at varying levels and degrees of proficiency, depending on such factors as professional integrity, background and training, and understanding or awareness of the scope and importance of the work they are engaged in. Unfortunately, these informal efforts at quality control are often inadequate and usually fail to provide adequate documentation.

Because of the routine nature of the normal workload, or, perhaps, the pressures of occasional high-priority "rush" projects, quality control can be neglected easily.

Therefore, in order to assure validity and reliability of the final results, it is imperative that each agency require a specific control program for every sampling procedure and analytical test.

1.3 Objectives and Scope of These Guidelines

The objective of this document is to provide guidance or instruction for agency personnel at all levels to assist in the development or modification of quality control programs. The diverse functions of the many types of agencies that will use these guidelines necessitate some generalization; whenever possible, however, we provide examples to illustrate application of the principles cited. We attempt to answer such questions as:

1. "Are the data valid?"
2. "Are they good enough for the intended use?"
3. "Is the technical services group performing consistently?"
4. "How can we be sure that our equipment is capable of providing correct results and is operating so that it does?"
5. "How should we document or demonstrate our level of performance to others?"

In the following pages Section 2 describes the major characteristics of quality control, indicating the types of activities available for incorporation into a quality control program. Sections 3, 4, and 5 deal with atmospheric monitoring, source monitoring, and laboratory operations, respectively, considering for each of these functions three major phases of quality control:

- Control of physical parameters
- Analysis of the measurement process
- Documentation and demonstration of quality control.

Section 6 describes the basic techniques of data handling and data evaluation, particularly as they are applied in air pollution control laboratories.

2.0 THE MAJOR ELEMENTS OF QUALITY CONTROL

The major elements of a quality control program can be considered broadly in two categories: control of the physical parameters and analysis of the total measurement process. We differentiate these two aspects of quality control chiefly as an aid to understanding. Control of physical parameters entails such functions as calibration, maintenance, and standardization of materials. Analysis of the total measurement process is a management tool for continuous evaluation of the performance capability of a technical services laboratory and of the data the laboratory produces. In this context analysis encompasses such laboratory evaluation techniques as analyzing spiked samples, replicate analysis, and interlaboratory comparisons, and the associated statistical interpretation of the data. We may say, then, that control of physical parameters is designed to reduce the frequency of occurrence of errors in laboratory operation and that procedures analysis is applied to determine the effectiveness of the physical control measures. An effective quality control program requires both kinds of effort, aimed at one goal: the generation of valid data. Figure 2.1 illustrates how each category relates to each of three phases of the total sample analysis system:

- Sample collection
- Sample analysis
- Data acceptance and performance evaluation

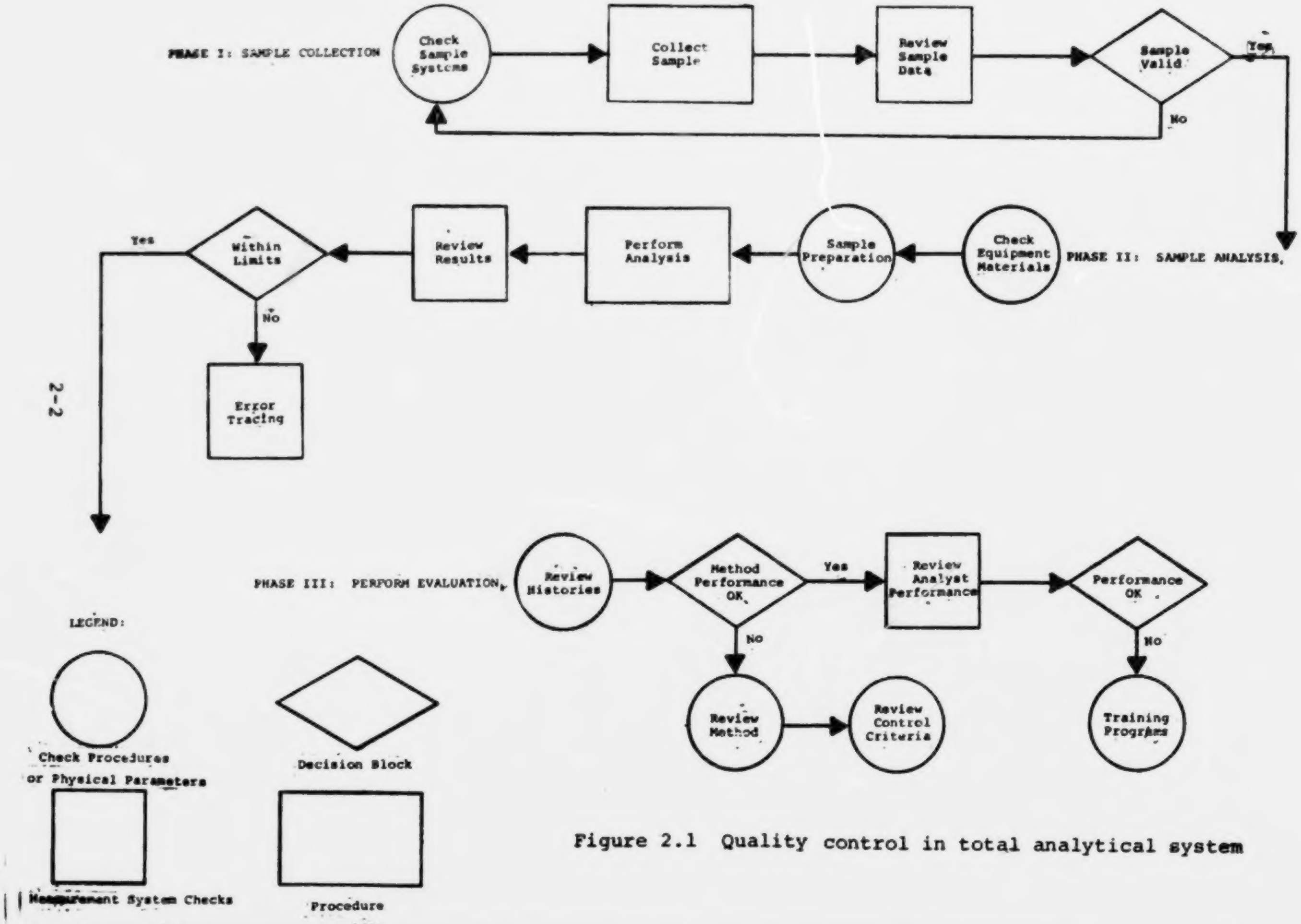

PHASE I: SAMPLE COLLECTION
Check Sample Systems
Collect Sample
Review Sample Data
Sample Valid
Yes
No
PHASE II: SAMPLE ANALYSIS
Check Equipment Materials
Sample Preparation
Perform Analysis
Review Results
Within Limits
No
Error Tracing
Yes
PHASE III: PERFORM EVALUATION
Review Histories
Method Performance OK
Yes
No
Review Analyst Performance
Performance OK
No
Review Method
Review Control Criteria
Training Programs
LEGEND:
Check Procedures or Physical Parameters
Decision Block
Measurement System Checks
Procedure

Figure 2.1 Quality control in total analytical system

2.1 Controlling Physical Parameters

Control measures to assure the production of valid data can also be thought of simply as good operating practices, in both sampling and laboratory analysis. Although details vary with each laboratory and application, the practices usually considered are these:

- Calibration procedures
- Functional checks of components in the measurement system
- Scheduled preventative maintenance
- Nonscheduled maintenance
- Standardization of materials
- Control of interferences
- Recording procedures
- Batch-checking procedures
- Good housekeeping techniques
- Control procedures for auxilliary services

Examples of these procedures and criteria for applying them are given in the sections dealing with field and laboratory operations. Management of each technical services group will require decisions regarding which of these measures should be applied, how often, and specifically in what way (detailed protocol). Among the many elements that will influence these decisions are such practical matters as availability and cost of materials, availability and cost of manpower, logistics, scheduling, and legal requirements. Further, the choice of quality control methods will be influenced by final application of the data generated and by the results of the continuing second step in quality control: analysis of the total measurement system.

2.2 Analysis of the Total Measurement System

The effectiveness of the types of physical controls just discussed -- calibration, maintenance, standardization, and the like -- can be determined by a number of statistical and other techniques, including analysis of data and review of laboratory records and reports. Procedures for this type of detailed analysis are amenable to a systematic approach, we are speaking not about occasional, random spot-checks of laboratory data and staff performance, but about a continuous, orderly process of administrative analysis. Techniques of such analysis are discussed in detail and exemplified in later chapters concerning field and laboratory operations. At this point we consider only a few fundamentals.

2.2.1 Precision and Accuracy

The terms "precision" and "accuracy" denote specific, measurable characteristics of laboratory analysis. They are key concepts of quality control, defined as follows:

- Precision is a measure of the reproducibility of results.[1] It is determined by replicate analyses, and it represents the variability of results among those replicate analyses. Precision can be expressed as standard deviation, variance, or range.

- Accuracy is the difference between a measurement and an accepted value.[2] Accuracy represents the magnitude of error in a measurement. It is expressed either as relative error in percent or in concentration terms such as parts per million. Accuracy is determined by comparing analytical results from analysis of unknown samples to results from analysis of reference materials.

Most of the critical parameters in an analytical system should be evaluated in terms of precision and accuracy. If they are not obvious, these critical parameters can be identified through sensitivity testing.

2.2.2 Control Chart Techniques

Several techniques are available for plotting control charts of accuracy and precision. Choice of a technique for computing precision depends primarily on the change in reproducibility as a function of change in the parameter being measured. Chapter 5 represents a method for determining the type of precision control chart to be used in a given situation.

Choice of a technique for expressing and for plotting accuracy data on a control chart depends on the nature of the sample, interferences, and the sensitivity range of the method. The techniques used to determine accuracy are:

- Analysis of primary or working standards.
- Spiked samples.
- Percent recovery calculations.
- Standard additions

The major difference between precision control charts and accuracy control charts is that precision charts show variability between sets of measured values, whereas accuracy charts show variability between measured values and known values.

To enhance the reader's understanding of the statistical terms that are used in discussing accuracy and precision in later chapters, we provide some important definitions:[1,2,3,4,5]

- Measures of Central Tendency - Parameters such as the arithmetic mean, geometric mean, median, mode, etc. which are used to describe the point about which the data tend to cluster.

- Arithmetic Mean - The most commonly used measure of central tendency is the sum of the values of the observations divided by the number of observations.

$$\text{Population Mean} \quad \mu = \frac{1}{N} \sum_{i=1}^{N} X_1 \quad i = 1,2,3,\ldots,N$$

where N = Number of observations in total population

X_i = Observed values

- Frequency distribution - Grouping observed values into specific categories.

- Normal distribution - The bell-shaped probability distribution which is determined by two parameters, i.e. the mean and the standard diviation.

- Variance - A measure of the variation of individual observations about the mean. The variance of the population and of a sample are σ^2 and S^2 respectively.

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^{N} (Xi - \mu)^2 \quad i = 1,2,3,\ldots,N$$

where σ^2 = variance of population

X_i = observed values

μ = population mean

N = number of observations in total population

$$S^2 = \frac{1}{N-1} \sum_{i=1}^{N} (X_i - \bar{X})^2 \quad i = 1,2,3,\ldots,N$$

Where S^2 = variance of sample

X_i = observed values

$\bar{X}$ = sample mean

N = number of observations in the sample

- Standard Deviation - A measure of the variation of individual observations about the mean. The unit of measurement for the standard deviation is the same as that for the individual observations. The standard deviation (equal to the square root of the variance) is referred to as σ and S for the population and a sample respectively.

- Random Error - Repeated analyses to determine the concentration of a contaminant in a sample will usually result in different values. These values, which tend to cluster about the true value, are caused by indeterminate errors. The distribution of random error is generally assumed to be normal with a mean equal to the true value and a variance of σ^2.

° Bias - The result of a determinate (but possibly unknown) source of error which causes the result of an analysis to be above or below the true value. Typical sources of bias include; improper calibration, human error in reading a meter or a color change.

° Range - The difference between the maximum and minimum values for a sample of observed values. When the number of observed values is small, the range is a relatively sensitive measure of general variability. As the number of observations increases the efficiency of the range (as an estimator of the standard deviation) decreases rapidly.

° Coefficient of Variation - The ratio of the standard deviation to the mean, also referred to as the relative standard deviation. It is usually expressed as a percentage and is given by

$$CV = \frac{S}{\overline{X}} (100)\ \%$$

where S = standard deviation of a sample

$\overline{X}$ = mean of a sample

° Confidence Interval - A statistic (e.g. the mean $\bar{X}$) is computed from the data for a sample. The statistic is then used as a point estimate of the population parameter (e.g. the mean μ). It is recognized that the statistic computed from a second sample would not be identically equal to that for the first sample. Because of this points A and B are determined such that it can be said with a specified probability that the true value of the population parameter lies within the interval described by A and B.

For example the probability statement for the 95% confidence interval estimate of the population mean is given by;

$$P_r\left(\bar{X} - \frac{t_{n-1}S}{\sqrt{n}} < \mu < \bar{X} + \frac{t_{n-1}S}{\sqrt{n}}\right) = 0.95$$

where $\bar{X}$ = sample mean

S = sample standard deviation

t_{n-1} = Student "t" value for n-1 degrees of freedom

n = number of observations in the sample.

The probabilities usually associated with confidence interval estimates are 90%, 95% and 99%. For a given sample size the width of the confidence interval increases as the probability increases.

- Confidence Limits - The end points of the confidence interval A and B as discussed above, where:

$$A = \bar{X} - \frac{t_{n-1}S}{\sqrt{n}}$$

$$B = \bar{X} + \frac{t_{n-1}S}{\sqrt{n}}$$

° "t" Distribution - A probability distribution developed by W. S. Gosset (writing under the pseudonym "Student") used in the computation of confidence interval estimates when σ (the population standard deviation) is unknown. In such a case S (the sample standard deviation) is used as an estimate of σ. When the sample size is small the value of "t" for a given probability level differs significantly from the "z" value for the normal[5] distribution. For example in determining the 95% confidence interval estimate of the mean when the sample size was 10, the value of t is 2.262 whereas the value of z from the normal distribution is 1.96 (regardless of sample size).

° Adjustment Factors - Adjustment factors as applied in the manual are multipliers used to calculate statistical control limits for control charts. They provide a method of approximating the distribution of all the values in the universe when calculating statistical limits. This is necessary because the distribution of sample values differs from the distribution of universe values. The factors used in this manual are D_3, D_4, B_3, B_4, and A_2. Definitions of these factors and formulae for computing them are in Appendix A. Tables with the factors used for the 99% confidence interval are in Appendix B. The application of each of the factors is:

- D_3 - Compute the lower control limit for a range control chart.
- D_4 - Compute the upper control limit for a range control chart. In some cases, D_4 can be used for the lower control limit also (see Section 5.3.6).
- B_3 - Compute the lower control limit for standard deviation or coefficient of variation control charts.
- B_4 - Compute the upper control limit for standard deviation or coefficient of variation control charts.
- A_2 - Compute upper and lower control limits for average control charts.

2.2.3 Review and Control Procedures

Non-statistical review procedures are also required for determining validity of data. These include procedures for evaluating personnel performance, instrument performance, and quality of reagents and materials.

Procedures for checking the performance of laboratory analysts include round-robin tests, both intra-laboratory (between individual analysts or groups) and inter-laboratory (between members of different organizations). Inter-laboratory proficiency testing can be applied to both field sampling and laboratory analysis. For determining trends in individual performance over a long period of time, control charts showing the accuracy or precision of the results obtained by a single analyst using a specific analytical method can be useful.

Procedures for review and control of instrument performance include review of maintenance logs and function check data and the establishing of control limits for calibration curves. Procedures are also required for checking automatic recording and transmission equipment.

Review and control procedures for checking quality of reagents and materials include scheduled batch checking and restandardization.

3.0 QUALITY CONTROL IN ATMOSPHERIC SAMPLING

Attaining the highest possible quality of data from an atmospheric monitoring program requires good operating procedures and methods of determining the level of quality achieved. Quality control procedures for atmospheric monitoring in the field are different from those for laboratory analyses, because of different operating conditions. Further, air monitoring does not involve uniform samples, the concept of sample replication is not easily applied, and the occasional use of unattended automatic instruments in remote locations may complicate the application of quality control techniques. In field operations the major application of statistical techniques is for determining that the operational variables of analyzers and samplers are within acceptable limits. The most important control variables for which criteria should be adopted are:

- Sample and reagent flow rate
- Span and zero drift
- Output noise
- Instrument response time
- Recorder dead band
- Sample conditioning
- Environmental conditions
- Power supply
- Response to functional tests

Standard procedures should be established to control these parameters. Also, output data may be checked for extreme values, and the total performance of an analyzer may be measured in terms of its output of good data as a proportion of total in-place operating time.

This chapter discusses quality control procedures common to all phases of air quality monitoring, including monitoring systems and integrated or static monitoring techniques.

3.1 Controlling the Physical Parameters

3.1.1 Environment

Air sampling is conducted under a variety of environmental conditions: monitoring sites range from fixed, ground-level, enclosed (interior) stations controlled for temperature and relative humidity and having adequate, well-regulated power supplies to outdoor stations located at various altitudes and exposed to widely ranging temperatures, possibly mobile platforms mounted in aircraft or vans. These environmental factors can affect the reliability of the sampling device and the quality of the data obtained. Table 3.1 lists some of the more important environmental influences cited by the International Electrotechnical Commission[6] and some possible effects of variation. In atmospheric sampling, each sampler and instrument used should be examined for these and other possible environmental effects with particular attention to those mentioned in methods descriptions and listed by manufacturers. Every attempt should be made to adhere to absolute limitations

TABLE 3.1

ENVIRONMENTAL INFLUENCES AND EFFECTS

Influencing Factors	Effect
Ambient Temperature	Sample and reagent flow rates, life of electronic components, amplifier drift, motor performance, ink drying, reagent evaporation
Barometric Pressure	Mass flow rate of air sample, requires correction to m.s.l. pressure in reporting mass concentrations of contaminants
Vibration and Shock	Alignment of optical components, joint leakage, microphony in NDIR analyzers, damage to fragile components, recorder pen movement
Electric Fields	Interference in electronic signal processing
Voltage	Performance of voltage sensitive electronic components, motor speed
Frequency	Speed of synchronous motors (chart speed for example), performance of frequency-dependent amplifiers

and, where necessary, to make operating adjustments and calculation corrections that will account for non-controllable variations. Examples of such practices include the calibration of rotameters with regard to temperature (particularly those used to meter reagent flow) and the correction of contaminant concentrations reported in mass units for pressure variation.

Good housekeeping is as important at air monitoring sites as it is in laboratory operations in that it provides the proper setting for an effective quality control program. Although some of the effects of poor housekeeping may seem indirect or may seem more related to occupational safety and health than to system performance, they usually entail poor maintenance and so a reduction in the quality of data. Some elements of poor housekeeping practices and possible adverse effects are given in Table 3.2.

3.1.2 Reagents and Supplies

Most of the relevant information on quality control as related to reagents and supplies is presented in Chapter 5. Several important points relating to air monitoring are emphasized here. These include provision for proper transport of reagents in the field and periodic checking of reagents that are held in instrument reservoirs or that are regenerated in situ. Some important reagent checks are pH tests, visual clarity, and efficiency of dye or color re-

TABLE 3.2

EFFECTS OF HOUSEKEEPING PRACTICES ON SYSTEM PERFORMANCE

Element	Possible Effects
Excess atmospheric or accumulated dust	Failure of electrical contacts and switches, excessive wear of mechanical components, excessive soiling of optical components
Reagent spillage or leaks	Corrosion, hazardous vapors, electrical hazards, insecure footing
Improper maintenance of air conditioning equipment	Air conditioning failure, operation outside of designated limits, equipment damage, freezing, inking pen failures, excessive reagent evaporation
Improper use of extension cords or overloading of circuits	Poor voltage control, excessive circuit failures, electrical hazard
Improper cleaning of glassware and reagent containers	Reagent contamination
Non-systematized storage of parts and tools	Loss of tools, absence of tools and parts when required, subsequent system failure

moval by carbon columns. Procedures for checking reagents and schedules for their replacement or regeneration should be documented and followed.

Filter media can be classified as reagents. Random sampling schemes for checking new lots of filter media can be established to measure flow characteristics, surface uniformity, presence of pinhole leaks, pH, ion blanks, and light reflectance or transmittance characteristics. Acceptance criteria should be related to the use of the media. An example of an acceptance sampling scheme is presented in Chapter 6 for data checking. The same kind of sampling design can be applied to media. As a practical consideration such tests as checking for pinhole leaks in glass fiber filters should be performed in the laboratory on every filter to be used in the field. Acceptance testing becomes practical only when the number of acceptance criteria is large enough to make testing of each item costly or time consuming.

3.1.3 Calibration Materials

Calibration materials, primarily gases, are introduced into air monitoring devices in known quantities so that the analyzer signal output can be related to the concentration of the contaminant in the sample stream. Calibration gases may be obtained commercially or generated on site. In either case the major concern in quality control is the degree of accuracy obtainable with the calibration.

Secondary considerations are stability of output, effect of storage, effect of operating conditions, and verification of standards.

Commercial calibration gases are usually obtained in pressurized cylinders. They are most often used "as delivered", or they may be diluted on site. Because statements concerning preparation tolerance and analysis accuracy vary among suppliers, it is useful to define the term "calibration gas" and to use the definition in procurement and validation. One useful statement follows:[6]

> "For purposes of spanning operations, these gases represent conventionally true values against which indicated values are compared. Therefore, the calibration gases should be traceable to standards agreed on by the user and the supplier or to national standards, and the uncertainty of the conventionally true values should be stated."

New certified cylinders of calibration gases should be obtained before depletion of existing cylinders so that cross-checks can be made. If results indicate uncertainty, additional interorganization cross-checks or comparison testing may be required.

Experience has shown that true "zero" gases can be as difficult to obtain as true "calibration" gases, and their use requires the same precautions. Increasingly, calibration gases are being generated on site. One rapidly developing technique is the use of permeation or diffusion sources.

This technique usually involves the permeation of a pure gas through a semi-permeable material (such as Teflon) from a liquefied quantity of the gas encapsulated under its own vapor pressure in a container having at least one surface of the semi-permeable material. The pure gas is diluted by a carrier gas flowing at a known and precisely controlled rate. The rate of permeation is temperature-dependent and must be known. One advantage of the technique is that the rate of permeation can be verified by determining the weight loss of the permeation source.

Ozone must be generated on-site, by passing oxygen or air over an ultraviolet source. At the present state of development, a referee analysis must be performed.

Regardless of the type of calibration material, an effective quality control program requires accuracy levels with these materials that are consistent with the method of analysis. Methods specified by the Environmental Protection Agency and most other published methods will include statements of the accuracy and replicability to be expected. Obviously, the accuracy of the calibration materials must be greater than the overall accuracy expected. The stated analysis accuracy of calibration sources should be ±2% of the true value.

3.1.4 Calibration and Maintenance Procedures

Calibration - Specific calibration procedures are described in both official and unofficial documents.[7,8,9] Procedures specified for the method or analyzer in use should be followed. The frequency with which calibrations are performed will affect the confidence limits of the data, depending on the degree to which calibration curves change with time. Initially the maximum time intervals between calibrations may be set by determining what regulatory requirements apply, as given, for example, in the surveillance portion of an implementation plan. This minimal schedule will, of course, be modified by resource and logistical constraints such as total available manpower, manpower time required for each calibration, station siting (e.g. distance from central laboratory), and required laboratory assistance.

Each technical services organization should develop a history of the replicability of calibration runs and of the expected change in the calibration curve with time. On the basis of such records, operators can determine the acceptability of a single calibration and perhaps modify the calibration schedule.

Generally, calibration records should include space for the following information:

- Instrument identification (serial or other identification number)
- Date
- Operator identification
- Calibration technique
- Description and identification of standard material used

- Test or other code - for use in identifying samples for referee analysis
- Operator comments
- Data

Example - In calibration of a nondispersive infrared carbon monoxide analyzer, the following procedure might be used:

- Conduct functional checks described in the operator's manual to be certain the analyzer performs within specifications.

- Obtain five cylinders of carbon monoxide zero and calibration gas covering the range of 0-90% of full scale and including the zero gas and the 90% of full concentration. The stated concentrations should be known within ±2% of the true concentration.

- Span and zero the analyzer using the zero gas and the calibration gas closest to 60% of full scale concentration. Adjust the zero and span controls so that the recorder values correspond to the specified cylinder values.

- Introduce the other calibration gases sequentially, allowing the analyzer to reach a stable value before changing cylinder sources.

- Plot the recorder scale values against the stated values.

- Repeat steps 3 through 5.

- Inspect the calibration plots. If both plots indicate that any one span gas deviates from an otherwise smooth curve that could be drawn between the remaining points, recheck that calibration gas. If a smooth curve can be drawn through at least one plot, proceed to analyze the difference between duplicates.

° The acceptability of the calibration precision can be determined with a control chart for Range. For this instrument the control limits are $\bar{R} \pm 3\sigma/\sqrt{n}$, where $\bar{R}$ = average value of the Range (in the case of duplicates this is equal to the difference between the two values). Charts have been tabulated to give the estimate of σ in terms of R.[10] The upper and lower control limits are $D_4\bar{R}$ and $D_3\bar{R}$ respectively. D_3 and D_4 for duplicates are found in these tables to be $D_4 = 3.267$ and $D_3 = 0$. The central line is $\bar{R}$. After the control chart has been prepared the values of the Range are plotted by successive sub-groups (each set of duplicates). If the values for R fall within the control limits the replicability or precision would be judged to be within control. As technical personnel gain experience with a particular instrument, they may desire to establish new limits for the calibration curve. The decision will be based on results of periodic recalculation of the standard deviation of the Range. An example of how control limits for a calibration curve are calculated is shown in Appendix C.

° Record all data pertinent to the calibration. Take action to implement the use of a new calibration curve if changed.

° Introduce calibration gas to be used in routine span operation and note scale value. This value will be necessary for proper setting of the span control in future routine operations until a new calibration is performed.

Other types of calibration may be performed such as in those other dynamic systems utilizing on-site generation of calibration gases through use of permeation tubes, ultraviolet generation of ozone, and other physical or chemical processes. Still other forms of calibration include those which are designed to calibrate the detector portion of the analyzer only. These are sometimes referred to as "static" or "reagent" calibration techniques. Regardless of the form of calibration, a history of calibration data should be developed such as described in the preceding paragraphs. The data collected on replicate sampling during calibration can be used to determine whether or not the analyzer or sampler is performing according to expected or required specifications and to determine the frequency with which calibrations must be performed in order to keep within performance specifications of the method.

Maintenance - From the standpoint of quality control, proper maintenance of air monitoring equipment should improve the quality of data and increase the recovery rate of valid data. Servicing and maintenance schedules should relate to the purpose of the monitoring, the environmental influences, the physical location of analyzers, and the level of operator skills. Data provided by instrument manufacturers and the EPA "Field Operations Guide for Automatic Air Monitoring Equipment"[7] are useful in developing an initial maintenance program. Most such manuals present instructions for general service and for service oriented to specific instruments. They further indicate the recommended time intervals for various types of service, such as tasks to be performed daily, semi-weekly, bi-weekly, monthly, quarterly, and semi-annually.

Example. Schedule for Daily Servicing - General

- Upon arrival at the monitoring site observe all recorders for indication of normal operation.
- Check liquid traps in instruments and probes.
- Check for broken sample lines; check condition of probe or sample line filters.
- Check all connections for possible leaks.
- Check for chart supply and replace charts where needed.
- Check for timing of all charts, timers and clocks.
- Check all flow-rate indicators for proper flow.
- Check all rotameters for dirt and water, particularly adjacent to ball. Clean and dry if necessary.
- Check sample conditioning apparatus.
- Service inking pens where required.
- Check for reagent supply on all wet chemical analyzers.
- Check level of reagent in all lines, reservoirs, etc. on wet chemical analyzers. Check for evidence of carryover.
- Check gas cylinder pressure.
- Check for noisy or leaking pumps. Lubricate where required.
- Check recorder dead zone on all recorders. Note where checked.

- Check sampling schedule for static or intermittent sampling devices and operate as required.
- Record all maintenance and adjustments on log books or forms as specified.
- Record parts and supplies used on reorder form.

Service and maintenance should be performed by personnel according to skills and staffing pattern. In general, station operators perform routine servicing and trouble shooting tasks; they should not attempt repairs for which they lack the proper training or equipment, or for which the time required would interfere with other scheduled operations.

3.1.5 Design and Maintenance of Probes and Manifolds

The sampling of gaseous or particulate air contaminants range from exposure of a static (passive) device (such as a lead peroxide candle) through sampling from individual probes and shelters, to sampling with common probes and manifolds using an auxiliary air-moving device. Various probe designs in common use have been summarized and recommendations given to assure that the air sample reaching the analyzer or sampler is altered minimally.[7] After an adequately designed sampling probe and/or manifold has been selected and installed, the following steps will help in maintaining constant sampling conditions:

- Conduct leak test - Seal all ports and pump down to approximately 0.5 inch water gauge vacuum as indicated by a vacuum gauge or manometer connected to one port. Isolate the system. The vacuum measurement should show no change at the end of a 15-minute period.

- Establish cleaning techniques and schedules - A large-diameter manifold may be cleaned by pulling through it a cloth on a string. Otherwise the manifold must be disassembled periodically and cleaned with soap and water. Visible dirt should not be allowed to accumulate.
- Plug the ports on the manifold when sampling lines are detached. This will help to maintain the desired mass/velocity ratio.
- Maintain a flow rate in the manifold at 3 to 5 times the total sampling requirements or at a rate equal to the total sampling requirement + 5 ft^3/min. This will help to reduce sample residence time in the manifold and insure adequate gas flow to the monitoring instruments.
- Vacuum in the manifold should not exceed 0.25 inch water gauge. Keeping the vacuum low will help to prevent the development of leaks.

3.2 Analyzing and Controlling the Total Measurement System

Having applied all practical measures for control of the physical components of a sampling/analysis operation, the supervisor or manager proceeds with thorough analysis of the total measurement system in terms of quality control. He does this by applying several analytical techniques, which are described and illustrated throughout this manual. In this chapter the emphasis is on atmospheric sampling; the techniques presented here, however, such as the functional analysis described next, usually can be applied in other phases of technical services operations.

3.2.1 Functional Analysis

In application of quality control measures, the total measurement system can be viewed as a complex consisting of the analytical method, the instrument or analyzer, and the operator. The critical components of this complex are identified by functional analysis. We exemplify this technique as it applies to continuous monitoring, because continuous monitoring instruments do not provide a discrete sample with which to perform conventional statistical procedures, such as use of replicate analyses, spiked samples, and control samples.

A useful first step in functional analysis is to prepare a schematic diagram of the analyzer, identifying all major components and controls. Briefly summarize the theoretical principles of the measurement and indicate all algorithms and transfer functions relating the measured quantity to the final data statement of air quality, such as pollutant concentration. With this information one can identify the primary variables directly affecting instrument performance. Some of these variables include:

- Source output (active devices)
- Detector sensitivity
- Contactor efficiency (where reagents are used)
- Sample air flow rate
- Reagent flow rate
- Cell pressure (nondispersive infrared analyzers)
- Optical path length and alignment (colorimeters and spectrophotometers)
- Amplifier gain and stability
- Reagent quality

Next, extend the analysis to determine means for controlling these critical parameters and for detecting off-specification performance. Some parameters (such as flow rates and pressures) can be observed directly, but often one must monitor performance by observing secondary parameters that may indicate malfunction or off-specification performance. Such secondary parameters include:

- Signal output noise
- Span or zero drift
- Repetitive transient signals
- Time response to step input of contaminant
- Atypical appearance of charts
- Response to built-in function tests
- Physical appearance of reagent lines, reagent, and other components

Of these observable indicators of performance, the ones most adaptable to statistical monitoring are noise, span drift, and zero drift.

In contrast to continuous monitoring, batch or sequential monitoring (accomplished by collection of filter samples, use of impingers, or similar procedures) is much more closely related to laboratory procedures. Batch monitoring operations, like those in the laboratory, can be evaluated by use of replicate sampling, standard or spiked samples, and cross-checking among samplers or operators. Beyond these, however, a thorough functional analysis of the sampling and analysis procedures should be performed to identify critical operating parameters and sources of error, and to define what data histories are needed, how they shall be collected, and procedures for manipulating and interpreting the data.

An initial procedure in this functional analysis of batch monitoring might be to construct a flow chart of the sampling and analysis processes, identifying all performance criteria and control and measurement points. Calculations used in obtaining final results would be shown, as would information on expected repeatability and accuracy. Figure 3.1 illustrates a flow chart constructed for the determination of suspended particulate matter by the high-volume filter sampler method. The illustration indicates that flow rate, time of exposure, sample conditioning, and initial and final weights represent the critical parameters in the hi-vol method. Opportunities for cross-checking in the weighing operations also arise, and parallel sampling can be conducted.

3.2.2 Sensitivity Analysis

Following the functional analysis of the measurement system the technique of sensitivity analysis may be

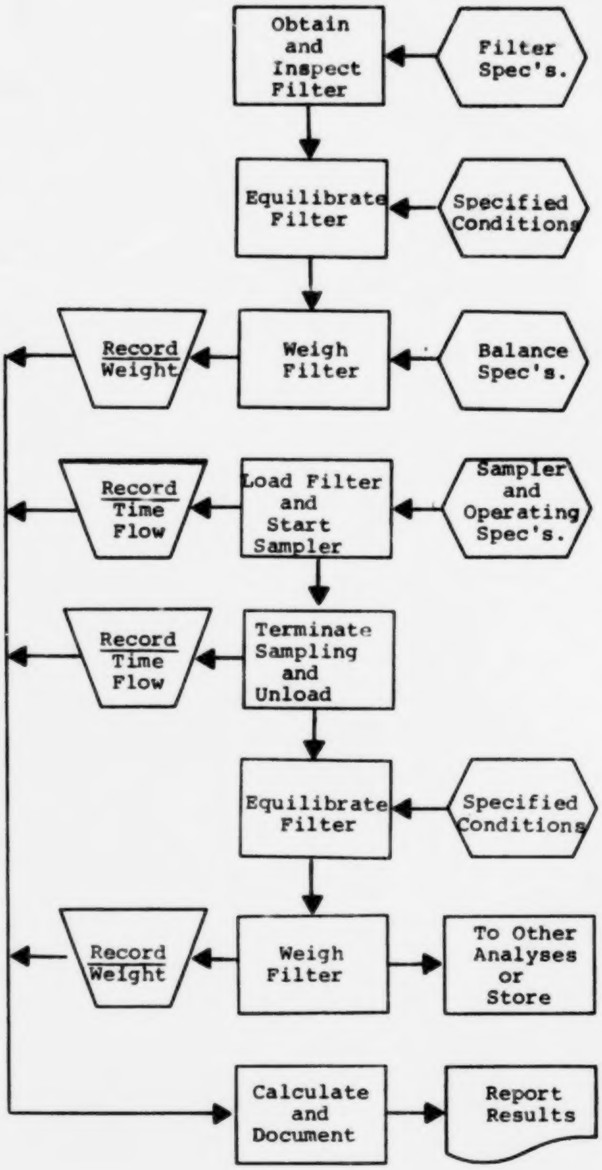

Obtain and Inspect Filter
Filter Spec's.
Equilibrate Filter
Specified Conditions
Record Weight
Weigh Filter
Balance Spec's.
Record Time Flow
Load Filter and Start Sampler
Sampler and Operating Spec's.
Record Time Flow
Terminate Sampling and Unload
Equilibrate Filter
Specified Conditions
Record Weight
Weigh Filter
To Other Analyses or Store
Calculate and Document
Report Results

Figure 3.1 Functional analysis of high volume suspended particulate sampling.

used to determine the effect of variations in either primary measurement control variables or in secondary influences or interferences. Sensitivity is defined as the partial derivative of a system output with respect to input. In a complex system a more practical definition of sensitivity, often employed for analytical purposes, is the incremental change in output resulting from an incremental change in input.

If the system can be described in terms of a mathematical model, an analytical approach may be taken usually utilizing a factorial design. In the control of air monitoring systems an empirical approach to sensitivity testing is more likely.

Example

Excessive zero drift has been detected in a continuous air monitoring instrument, but no component failure is indicated. Knowing the analyzer, the operator suspects that temperature or voltage variations may be influencing the instrument behavior. The operator wants to know how the voltage and temperature interact. Because the number of variables is small he could select a full factorial design of an experiment designed to test each variable at three levels - (1) within specified normal range, (2) above normal range, and (3) below normal range. The total number of experiments required would be p^n where

n = no. of factors = 2
p - no. of levels = 3

or $3^2 = 9$. The experiments can be identified as T_1V_1, T_1V_2, T_1V_3, T_2V_1, T_2V_2, T_2V_3, T_3V_1, T_3V_2, T_3V_3 where T and V refer to temperature and voltage respectively, and the subscripts refer to the level. Other tests, such as Youden ruggedness testing, could be used if the number of factors and/or levels is large. Fewer tests would be required than with the above technique, but the results would be nearly the same.

If an analysis of the data shows a relationship between one or more of the influence parameters and the dependent variable, in this case zero drift, a case would be made for better control of that parameter.

3.2.3 Compiling and Using Data Histories

In a quality control program, positive steps should be taken to provide methods, equipment, facilities, staff, and operational procedures that make possible the production of high quality data. Means of measuring performance and detecting promptly any deviation from acceptable performance should be adopted. Corrective actions in the event that data quality falls outside acceptable limits should be defined. Adequate data histories must be available with which to verify statements concerning the quality of the data.

In addition to the calibration data described earlier data histories should be collected on all of the critical measures of performance identified in the functional analysis.

Data histories most commonly kept are those for sample air and reagent flow rates, results of span and zero checks, results of use of other standards or function tests, noise, response time, and recorder dead zone. For example, if the specification for zero drift for a continuous analyzer is that it not exceed 1% of full scale/24 hours, and if the data acceptance criteria are set to reject all data recorded during a period in which the total drift exceeds 2% of scale, then an initial schedule might be set for zero checking once every two days. Experience may require adjusting the checking interval.

Use of data histories in maintaining quality control is based on the recognition that no analytical method or instrument yields perfect results; when repeated determinations are made on the same sample, some variation in results is inevitable. Even if all identifiable or assignable causes of variation are removed, some indeterminate sources remain. These indeterminate errors should be randomly distributed. Since the behavior of these random events can be predicted statistically, limits within which repeated measurements should fall can be computed. The design and use of control charts and other uses of data histories rely on the computation of these 'control limits'. It should be understood that even though application of statistical techniques indicates that an analysis or air monitoring process is in a state of control, this does not mean that every analysis or element of data is acceptable. Nor does it mean that the control limits are rigid; they can be adjusted to produce higher quality data.

As discussed earlier, replicate analysis cannot easily be applied to automatic continuous analyzers, and quality control of the data they produce must usually be based on maintaining performance characteristics within limits. One important indication of low-quality data from a continuous analyzer is excessive zero or span drift. Drift affects the quality of data because the calibration curve has been altered without the data reduction process having been automatically altered at the same time. Within pre-set limits it is possible to interpolate between the expected and the altered calibration curve if the altered curve can be identified. This is done by field operations known as zeroing and spanning, during which a known zero gas and a single calibration gas are introduced to the analyzer. The scale value is noted and compared with the value expected on the basis of the most recent full calibration. In effect two calibration curves are available, one representing the start of the time period immediately following the previous standardization and one for the time of the current standardization. If the change is not too great, a linear interpolation between the two curves is performed for data points between the two standardization operations. The difference between the succeeding span and zero readings is called span and zero drift and is expressed in terms of concentration per unit time, e.g. $\mu g/m^3$ per 24 hours.

One method of monitoring the state of control for span drift would be to construct a control chart for the mean span drift over some reasonable time period, perhaps two weeks. The center line for such a chart is drawn at the expected mean drift, μ, and the upper and lower limits will be $\mu + 3\ \sigma/\sqrt{n}.$ If the distribution of the span drift is normal, these limits should contain approximately 997 values out of every 1,000. If the subgroup span drift means are expressed as $\bar{x}$, the best estimate of μ is the overall sample mean, $\bar{\bar{x}}$, which may be computed from the subgroup means. If we have less than ten span operations during the two-week period representing the subgroup, then $\bar{R}/d_2$ is an unbiased estimate of σ. $\bar{R}$ is mean of the subgroup ranges. The factor $A_2 = 3/\sqrt{n} \cdot d_2$ has been compiled and listed in standard texts on statistics. Appendix A defines these factors. Table 3.3 lists the span drift data for an analyzer over 26 two-week periods. Since span checks were made every other day, seven checks were made every two-week period. Therefore

$$\bar{\bar{x}} = \frac{\Sigma\ \bar{x}}{n} = \frac{35.0}{26} = 1.35$$

TABLE 3.3

SPAN DRIFT FOR ANALYZER A FOR 26 TWO-WEEK PERIODS

Period	Mean Span Drift ($\bar{x}$)	Range (R)
1	1.4	0.8
2	1.5	0.9
3	1.3	0.6
4	1.4	0.8
5	1.2	0.9
6	1.3	0.6
7	1.2	1.1
8	1.4	1.3
9	1.3	0.4
10	1.2	0.3
11	1.8	0.6
12	1.3	0.9
13	1.4	1.1
14	1.2	0.4
15	1.5	0.7
16	1.2	0.8
17	1.1	0.8
18	1.3	0.7
19	1.2	0.2
20	1.4	0.5
21	1.6	0.7
22	1.4	0.9
23	1.5	0.8
24	1.3	0.9
25	1.2	1.2
26	1.4	0.4

Mean span drift ($\bar{x}$) = average span drift for a two-week period.

Range = Max-min values for a two-week period.

$$\bar{R} = \frac{\Sigma R}{n} = \frac{19.3}{26} = 0.74$$

$A_2 = 0.419$

A_2 is based on $n = 7$, the number of checks per two-week period.

$A_2\bar{R} = 0.419\ (0.74) = 0.31$

$\bar{\bar{x}} + A_2\bar{R} = 1.35 + 0.31 = 1.66$

$\bar{\bar{x}} - A_2\bar{R} = 1.35 - 0.31 = 1.04$

The information developed from Table 3.3 is plotted on the control chart shown in Figure 3.2. It is obvious that, except for only one two-week period, the analyzer operated satisfactorily.

Control charts for duplicate testing, such as might be developed for use with batch or intermittant monitoring, are similar to those described in detail in Chapter 5 on laboratory methods. Parallel sampling, such as might be done with high-volume particulate samplers and bubblers, can be analyzed by this technique.

A special control chart may be used for duplicates obtained in comparison testing. If it is assumed that this type of testing will be performed only at intervals, it may be difficult to obtain an unbiased estimate of the true expected difference, d, between duplicates on a control chart on which the central line is 0. Existence of bias can be determined from several indicators by using the method of extreme runs.[3] Bias is indicated by the following:

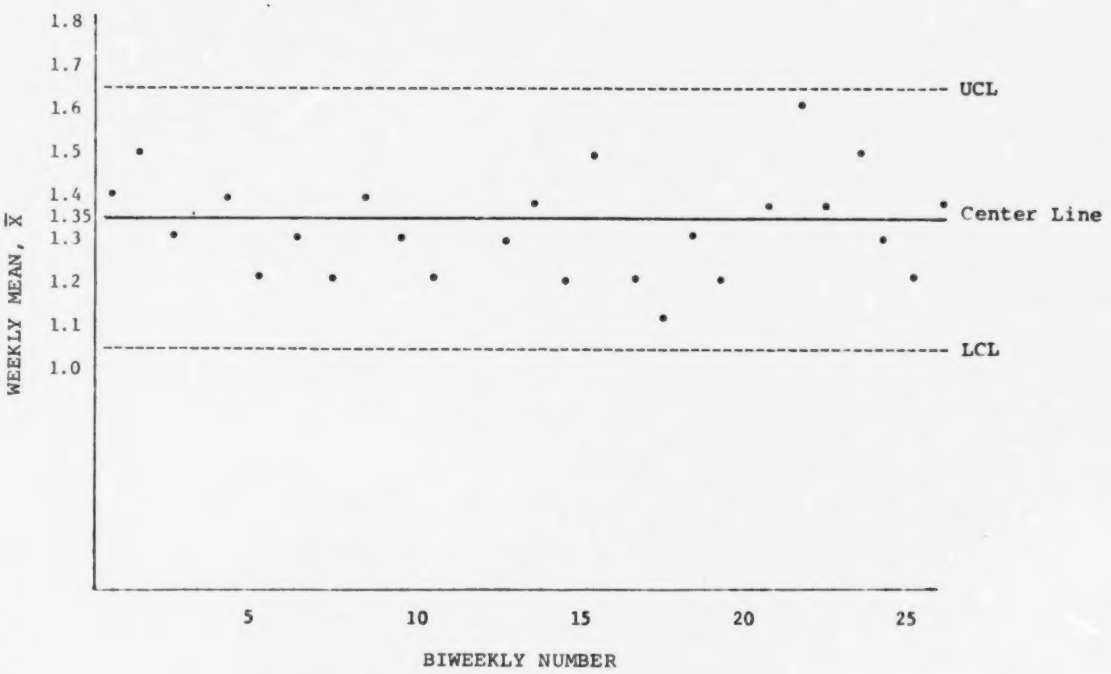


Figure 3.2 Control chart for span drift

- 8 successive points are on the same side of the central line
- 10 out of 11 are on the same side
- 12 out of 14 are on the same side
- 14 out of 17 are on the same side
- 16 out of 20 are on the same side

This type of chart is used, for example, in analyzing data collected by a mobile unit that regularly checks the air monitoring conducted at fixed sites. In this type of operation it is imperative that the mobile unit and the stationary instruments are sampling the same air mass.

3.3 Documentation and Demonstration of Quality Control

3.3.1 Records

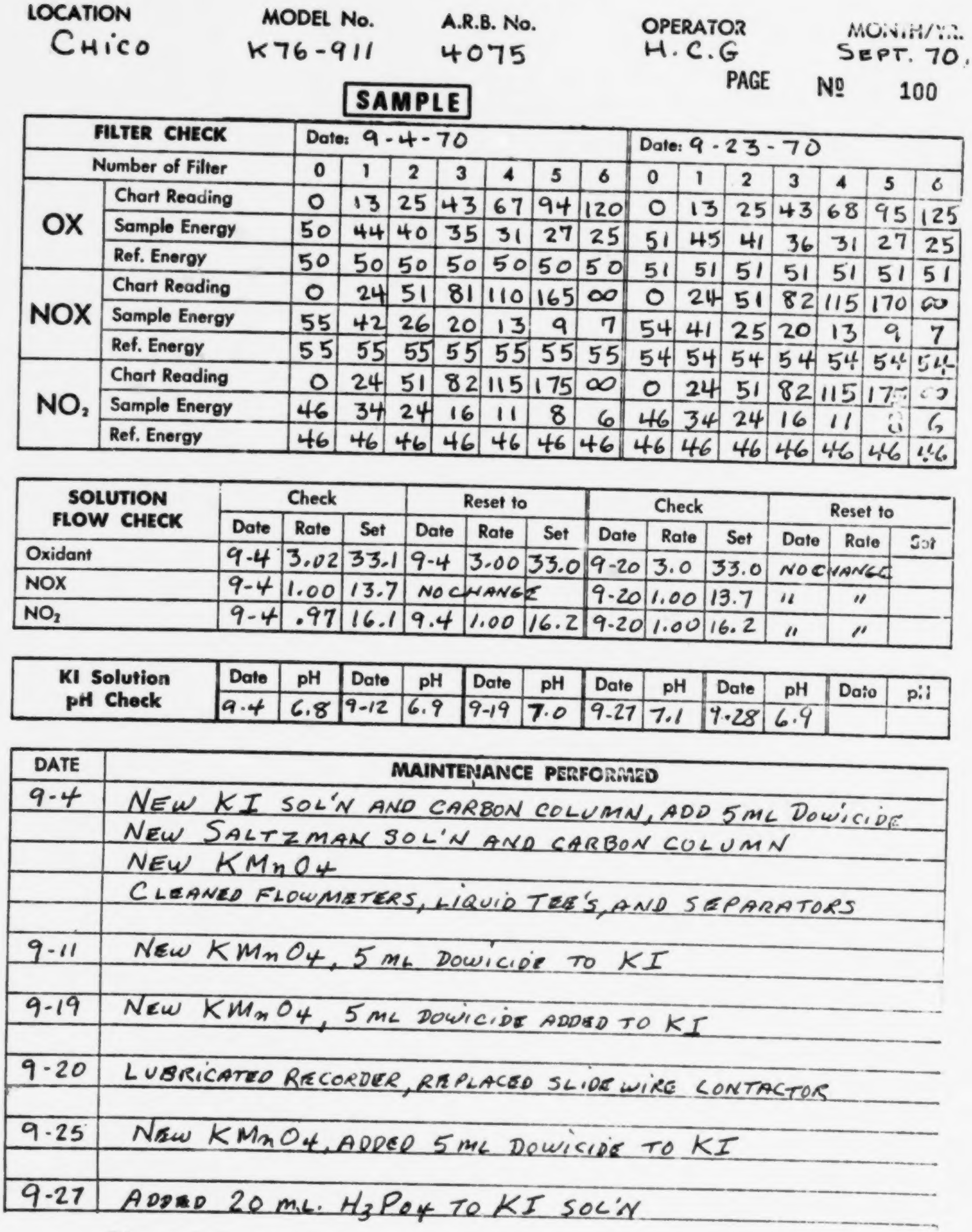
Administration of a quality control program requires adequate records needed to validate data prior to processing, to provide data histories, to aid in modification of service procedures and schedules, to develop records of parts usage, and to guide trouble shooting and repair. The general categories of these records are:

- Instrument service records - These may be in the form of lab books or prepared multiple copy forms. The California Air Resources Board has determined that the latter type better serves management functions. These forms provide space for entry of routine data such as flow rates, filter or span checks, reagent checks (such as pH of potassium iodide reagent for total oxidant), and maintenance performed. Similar forms could also include acceptable performance criteria for convenient reference by the station operator.

- Calibration records - These would contain all data applicable to calibration including certified analyses of cylinder gases; flow rates; results of referee or side stream analyses; recorder output data, including scale values; lag time, rise time, fall time; copy of recorder chart; gravimetric determinations, if any; temperatures; barometric pressure; and description of calibration procedures.

- Station log books - To include data on all station changes, station conditions, dates of supply delivery, subjective statements on air quality conditions, visibility observations, and notes of unusual events that might influence analyzer readings.

- Data validation and reduction notes - These would include all entries necessary for chart editing, including results of span and zero checks, flow rates adjustment, function tests, down times for service, and notes on known bad data. These entries may be made either on the chart or on special report forms. They are normally made on the chart for manual data reduction and on a special form for automated data reduction. In the latter case, the notes form a basis for supplementary computer instructions covering baseline data, span constants, and data to be excluded.



LOCATION	MODEL No.	A.R.B. No.	OPERATOR	MONTH/YR.
CHICO	K76-911	4075	H.C.G	SEPT. 70.

PAGE Nº 100

SAMPLE

FILTER CHECK		Date: 9-4-70							Date: 9-23-70						
Number of Filter		0	1	2	3	4	5	6	0	1	2	3	4	5	6
OX	Chart Reading	0	13	25	43	67	94	120	0	13	25	43	68	95	125
	Sample Energy	50	44	40	35	31	27	25	51	45	41	36	31	27	25
	Ref. Energy	50	50	50	50	50	50	50	51	51	51	51	51	51	51
NOX	Chart Reading	0	24	51	81	110	165	∞	0	24	51	82	115	170	∞
	Sample Energy	55	42	26	20	13	9	7	54	41	25	20	13	9	7
	Ref. Energy	55	55	55	55	55	55	55	54	54	54	54	54	54	54
NO_2	Chart Reading	0	24	51	82	115	175	∞	0	24	51	82	115	175	∞
	Sample Energy	46	34	24	16	11	8	6	46	34	24	16	11	8	6
	Ref. Energy	46	46	46	46	46	46	46	46	46	46	46	46	46	46

SOLUTION FLOW CHECK	Check			Reset to			Check			Reset to		
	Date	Rate	Set	Date	Rate	Set	Date	Rate	Set	Date	Rate	Set
Oxidant	9-4	3.02	33.1	9-4	3.00	33.0	9-20	3.0	33.0	NO CHANGE		
NOX	9-4	1.00	13.7	NO CHANGE			9-20	1.00	13.7	"	"	
NO_2	9-4	.97	16.1	9.4	1.00	16.2	9-20	1.00	16.2	"	"	

KI Solution pH Check	Date	pH	Date	pH	Date	pH	Date	pH	Date	pH	Date	pH
	9.4	6.8	9-12	6.9	9-19	7.0	9-27	7.1	9.28	6.9		

DATE	MAINTENANCE PERFORMED
9-4	NEW KI SOL'N AND CARBON COLUMN, ADD 5 ML DOWICIDE
	NEW SALTZMAN SOL'N AND CARBON COLUMN
	NEW $KMnO_4$
	CLEANED FLOWMETERS, LIQUID TEE'S, AND SEPARATORS
9-11	NEW $KMnO_4$, 5 ML DOWICIDE TO KI
9-19	NEW $KMnO_4$, 5 ML DOWICIDE ADDED TO KI
9-20	LUBRICATED RECORDER, REPLACED SLIDE WIRE CONTACTOR
9-25	NEW $KMnO_4$, ADDED 5 ML DOWICIDE TO KI
9-27	ADDED 20 ML. H_3PO_4 TO KI SOL'N

Figure 3.3 Instrument Maintenance Form - California ARB

In addition to the records mentioned, provision should be made for rapid notification concerning out-of-limits analyzer performance as detected by the station operator or, with telemetry, by the control center supervisor.

3.3.2 Reports

Reports prepared as part of a quality control program are usually summaries designed to inform administrative personnel as to the quantitative and qualitative level of performance of the air monitoring activity. These reports must be tailored to the size and complexity of the operation. Several types of reports that might be employed are described briefly.

° Calibration Report - This report should summarize calibration activities during the report period, including equipment calibrated, date calibration performed, time required for calibration, source of standards, techniques used, problems encountered, and indication of any change in calibration. Quality control charts are useful here.

° Maintenance Summary - This report should describe significant maintenance, not routine servicing. It includes such activities as replacement of major components and changes of the equipment. This report will aid in developing a history of parts used and operations performed, to serve as input for a preventative maintenance program.

° Data Recovery Report - This report describes the performance of the air monitoring activity in terms of useful data recovered. For each separate analyzer or batch sampler one can determine a theoretical maximum amount of data that should be available, based on time in place, sample schedule, and scheduled downtimes for calibration, span and zero checking, and preventative maintenance. This report would list the percent of data recovered for each analyzer and sampler, by location, for the report period involved. A monthly or quarterly report should suffice.

A control chart may also be developed to indicate whether instrument or station performance is within expected limits on the basis of valid data, expressed as a percent of data theoretically available. This is known as a control chart for percent valid data.[10] The following parameters are calculated:

$\bar{p}$ = mean percent valid data (in this case the overall mean determined from past experience on percent of valid data).

$100 \cdot \sqrt{\frac{\bar{p}\bar{q}}{n}}$ = standard deviation of percent valid data.

$\bar{q} = 1-\bar{p}$

n = number of hours in sample period, e.g. in one month.

For example, if a station is yielding 85% valid data out of a possible 100%, the following calculations would apply if the station had operated 720 hours during the period of interest:

$\bar{p} = 0.85$

$\bar{q} = 0.15$

$n = 720$

$\sqrt{\frac{\bar{p}\bar{q}}{720}} = 0.013$

UCL (upper control limit) $= 0.85 + 3\ (0.013) = 0.88$

LCL (lower control limit) $= 0.85 - 3\ (0.013) = 0.82$

The control chart in this case is plotted with $\bar{p}$ as the central line, and $\bar{p} \pm 3\sqrt{\frac{\bar{p}\bar{q}}{n}}$ as the upper and lower control limit lines. The percent valid data ($\bar{p}$) for the monthly subgroup is plotted on the y-axis, and the subgroup number is plotted on the x-axis. If n is reasonably large, as for example the number of hours in a month, the normal distribution is a good approximation of the binominal distribution. In this case the probability is only three in a thousand that a value of $\bar{p}$ will fall outside the control limits by chance.

4.0 QUALITY CONTROL IN SOURCE SAMPLING

4.1 General Considerations

Currently, application of basic quality control elements to source or emission testing is almost nonexistent. Although operators are usually careful to clean and calibrate equipment before testing, the equally or even more important phases of sampling, such as statistical test design, control of interferences from unknown compounds, and other steps to insure the efficiency of sampling procedure are often ignored. The primary reasons for this are lack of knowledge pertaining to emissions from specific sources and lack of background data on various source sampling procedures.

In spite of these difficulties, however, the technical services supervisor who is oriented toward quality control will work toward developing a set of systematic procedures that will assure the highest possible quality of source-sampling data. He will find that many of the basic concepts of quality control can be applied or adapted to source sampling. As an example, consider the instrumental sampling of emissions. Although most emission testing is currently accomplished by manual techniques, instrumental methods are being developed and in special cases have proved successful for determining a specific gaseous component in a 'clean' dry gas stream. For most instrumental methods, the same decisions and criteria for maintaining acceptable operation of atmospheric monitoring (see Chapter 3) will also apply to source sampling.

4.2 Controlling the Physical Parameters

4.2.1 Interferences

The goal of a source sampling team should be to collect, store, and transport to the analytical laboratory a sample that is as free as possible from interferences. The interferences most commonly affecting field samples are related to these factors:[11,12,13,14]

- Composition of probes
- Composition of collection media and filters
- Cleaning procedures
- Standardization of reagents
- Storage and transport of samples.

These factors are analyzed more fully in Table 4.1.

TABLE 4.1

ELEMENTS FOR CONTROL OF INTERFERENCES

Element	Control Consideration
Probes	Inert to gases sampled. Trial runs to test inertness in undefined environment. Temperature control.
Media and filters	Filter requirements. Non-reactivity of filters. Requirements for distilled or deionized water. Blank requirements.
Cleaning procedures	Inertness of cleaning solutions. Elimination of residues.
Standardization of reagents	Normality. Stability. Frequency of exposure. Storage requirements.
Storage and transport of samples	Inertness of containers. Elimination of atmospheric influences. Time required for transport and storage.

4.2.2 Sampling Rate and Sample Volume

The sampling rate must be known accurately in order to relate the amount of sample collected to the stack gas concentration. Direct displacement or totalizing meters such as dry or wet test meters are preferred, since they can accurately measure the gas volume even if the gas flow rate varies, and they do not require constant attention. Rate meters require careful measurement of total sampling time and constant observation to make sure the rate does not vary because of pressure changes in the sampling train. Table 4.2 compares the accuracies of various types of flow meters.

Evacuated tanks or flasks can also be used to determine the volume of gas sampled if the initial and final pressure and temperature in the tank are carefully measured and the tank volumes are known.

4.2.3 Equipment Maintenance and Calibration

The accuracy with which one can measure various emission parameters depends greatly on the accuracy of the instruments used in sampling procedures. Some of the common sampling components that require maintenance and calibration to assure maximum accuracy are Pitot tubes, manometers, thermometers, flow meters, and gas meters.

Rules for calibration of the various instruments used in source testing are not available in the literature. In

Table 4.2 FLOW METER TYPES AND ACCURACY

Type	Fluid	Principle	Application	Accuracy Range
Direct Measurement				
Gas Prover	G	Batch displacement	Calibration[1]	±0.2%
(inverted bell type)				
Frictionless Piston	G	Batch displacement	Calibration	±0.2%
Bubble Meter	G	Batch displacement	Calibration	±0.2%
Mass	L	Mass measurement	Calibration[1]	±0.1%
Fluid Dynamic Type				
Orifices[2]	G,L	Head loss	Continuous & Intermittent Sampling	±0.5% (max.)
Venturi Meter	G,L	Head loss	Continuous & Intermittent Sampling	±0.5%
Direct Displacement				
Wet Test Meter	G	Continuous displacement	Calibration	±0.5%
Dry Gas Meter[2]	G	Continuous displacement	Intermittent sampling	±1%
Cycloidal	G,L	Continuous displacement	Calibration	±1%
(Roots type)				
Piston Pump	L	Continuous displacement	Continuous sampling	±1%
Area Meter				
Rotameter[2]	G,L	Head loss	Continuous sampling	±1% to 10%

(1) Obtainable with NBS traceability

(2) Commonly used in field sampling work

practice, the measuring devices are calibrated against known quantities or against devices known to provide a higher degree of accuracy (see Table 4.2), and are then adjusted to read the correct value. If the device cannot be adjusted, it is replaced or used as a spare with an appropriate correction factor.

Following are guidelines to the effective maintenance and calibration of source sampling equipment:

- Pitot Tubes - Compare with a standard type pitot tube by inserting both Pitot tubes into a duct and measuring the velocity at a specified point. A correction factor is then calculated as shown in Table 4.3

TABLE 4.3

EXAMPLE DETERMINATION OF PITOT TUBE CALIBRATION

Standard Pitot reading		Type S Pitot reading		
H_o	$\sqrt{H_o}$	H_1	$\sqrt{H_1}$	Ratio $\frac{\sqrt{H_o}}{\sqrt{H_1}} = C_p$
0.3	0.5477	0.415	0.642	0.853
0.5	0.7071	0.700	0.837	0.844
1.0	1.000	1.44	1.200	0.833
				C_p = 0.843

H_o = Velocity head ("H_2O)
H_1 = Velocity head ("H_2O)
C_p = Pitot tube coefficient

- Manometers - Inclined and U-tube manometers give direct readings and do not require calibration. The manometer must be clean, air-tight, and filled with the liquid specified on the scale. Where transducers or gauges are used to measure pressure, they should be connected in parallel with a manometer and adjusted to read the same value.

- Thermometers - Bi-metallic dial-type thermometers are commonly used. These should be checked against a mercury-in-glass thermometer and adjusted to read correctly. All thermometers used in a sampling program should be checked prior to use and should be adjusted to the following limits:

  150° F. ± 2°

  150-500° ± 5°

  500° ± 10°

- Dry Gas Meters - A dry gas meter is calibrated by connecting it in series with a bell-prover, or wet-test meter. Meters should be calibrated before every test series and should be adjusted to read within 1% of the true value.

- Orifices, Rotameters, etc. - These devices are calibrated by connecting them in series with a more accurate volume meter, such as a wet-test meter. Calibration should be performed before every 10 months, depending on frequency of usage. Calibration curves with deviations of no more than 1% should be established for each device.

All sampling equipment must be cleaned carefully to prevent sample contamination. Dichromate cleaning solutions are recommended for cleaning glassware prior to beginning a test series. Complete rinsing with tap and then distilled water is suggested. For metal analyses, certain types of glassware should not be used and cleaning with nitric acid is recommended. The method description should include guidelines for choice of glassware.

4.2.4 Conducting the Emission Test

Before starting an emission test, the sampling crew should follow a series of preparatory steps designed to reduce or eliminate interferences from various sources. Checklists enable the crew to follow the standardized procedures consistently. The operators should maintain complete notes in the field. Checklists can include such data as the following:

- Preparation of water or reagent blanks.
- Cleaning of impingers, probes, collection vessels, etc.
- Confirmation of reagent grades specified in the method.
- Preweighing of filters.
- Checkout of heating or cooling systems for probes.
- Leak check of sample train.
- Identification or visual check of Pitot tubes, meters, thermometers.

Typical data sheets used in the field are shown in Figures 4.1 and 4.2.

After the preparatory measures, the principal quality control effort is directed toward preventing measurement errors. Stack sampling involves a number of physical parameters, and the errors of measurement associated with each parameter combine to produce an error in the calculated emission rate.

Measurement errors are of two types: bias and random. In bias errors, which usually result from poor technique or faulty equipment, the measured value tends to differ from the true value in one direction. Errors of this type can be minimized by proper calibration and adequate training. Random errors result from a variety of sources that cause the measured value to deviate in either direction from the

GAS SAMPLING FIELD DATA

Material Sampled For ______________________________

Date ______________________________

Plant ______________ Location ______________

Bar. Pressure ______________________________" hg

Ambient Temp. °F ____________ Stack Temp., °F ____________

Run No. ______________________________

Power Stat. Setting ______________________________

Filter Used: ____________ Yes ____________ No

Operator ______________________________

Time	Meter (Ft.^{3})	Flow Rate CFM	Meter Temperature °F

Contents

Impinger No. 1 ______________________

Impinger No. 2 ______________________

Impinger No. 3 ______________________

Figure 4.1 Field data sheet

GAS SAMPLING - EVACUATED FLASK

TEST NO. _________ DATE _____________ LOCATION ___________________

Type of Operation ____

Sampling Flask No. ____________ Flask Volume, V_o __________ ml

Volume of Reagent, V_R _________________ ml, Type of Reagent

Leg 1 _______

Initial Flask Vacuum, p_i Leg 2 _______ $P_i = P_b - p_i$ = ___________

Total _______"Hg

Leg 1 _______

Final Flask Vacuum, p_f Leg 2 _______ $P_f = P_b - p_f$ = ___________

Total _______"Hg

Initial Flask Temperature, T_i = ________ °F + 460 = _______°R

Final Flask Temperature, T_f = ___________ °F + 460 = _______°R

Barometric Pressure, P_b = _______________"Hg

Clock Time __________________

CALCULATIONS:

$$V_s = (V_o - V_R)\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right)(17.7)$$

Figure 4.2 Field data sheet

true value. They are caused by inability of the operator to read scales precisely, by the quality and sensitivity of the measurement device, and by uncontrolled environmental variables.

Application of standard statistical techniques has shown that the maximum error associated with determining an emission rate (product of concentration and total stack gas flow) is about 15%.[12,13] Under normal sampling conditions, with no bias in the readings due to faulty equipment or operator technique, an error of less than 10.4% can be expected 99.6% of the time. The most significant error associated with any one measurement involves reading the inclined draft gauge used to measure stack gas flow velocity head.

Another significant error can occur in measuring particulate concentrations. Particles are segregated at the sampling nozzle when the velocity of approach to the nozzle does not equal the velocity of the stack gas at the sampling point. This error varies with the size of the particles, as shown in Figure 4.3.

4.3 Analyzing the Total Measurement System

Although, as mentioned earlier, many statistical techniques of quality control cannot be applied to emissions testing, a basic and detailed analysis of the total sampling operation can aid the technical services staff in providing high-quality samples that yield reliable data.

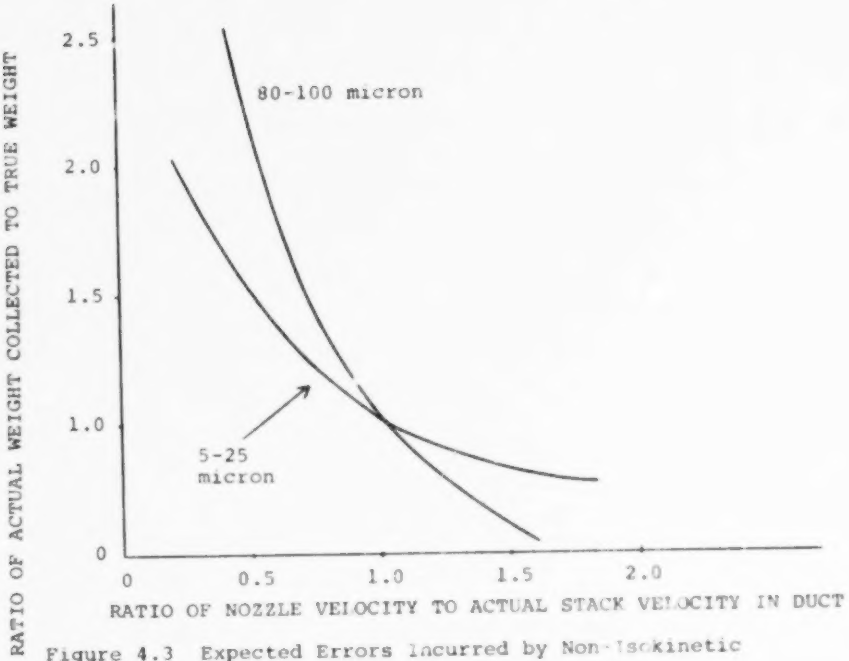


Figure 4.3 Expected Errors Incurred by Non-Isokinetic Sampling

(These data should not be used to correct concentrations obtained under non-isokinetic conditions since a wide variety of particle sizes is usually present.)

The emissions testing duties of a technical services group can involve a variety of sampling procedures related to the variety of sources that are monitored. Selecting the sampling method most appropriate is the first step in quality control. Among the factors to be considered are the major variables of the process to be sampled, location of sampling points, and size of the sample. Experience and judgement will influence method selection; review of method descriptions and consultation with others are often helpful, as are relevant literature sources such as those given in references 11 through 15.

Working within the framework of the method selected for a specific emissions test, one can proceed with analysis of the total measurement system. Prepare a schematic diagram of the sampling train; list the critical components of the system and note how their operation affects results. Set forth, as briefly and simply as possible, the theoretical principles on which the system is based.

These items should be prepared on paper for use by the technical services staff. The schematic diagram expresses relationships in visual form, showing how one element of a sampling/analysis system affects another. It displays opportunities for error, and therefore opportunities for control.

Systems analysis for quality control of emission testing should incorporate as many as possible of the elements described in Chapter 3 concerning atmospheric sampling and Chapter 5 concerning laboratory operations. Measures to assure quality of reagents, for example, are appropriate here. Compilation and analysis of data histories (such as calibration records) can lead to improvements in data quality. Documentation, by way of records, log books, summaries, and reports, can provide the information base required for quality control. Although performed in the field, often under conditions less formal than laboratory operations, competent source sampling requires the disciplined application of technical skills. In terms of quality control, 'stack sampling' represents a challenge to the technical services group: to develop attitudes, techniques, and detailed procedures that lead to consistent production of high-quality emissions data.

5.0 QUALITY CONTROL IN THE ANALYTICAL LABORATORY

5.1 Introduction

Laboratory quality control programs should include systematic procedures for performing analyses and for checking the level of performance for each method used. Statistical procedures are usually required for specifying performance standards, for recognizing analytical results that do not meet the standards, and for interpreting historical data. Standard operating procedures provide a base for achieving and maintaining a consistent level of analytical performance and for tracing errors when results do not meet the expected level. Standard operating procedures should be developed for each of the four major sources of analytical variation:

- Support services
- Reagents and materials
- Instrumentation
- Analytical technique

These may be considered as the chief physical parameters of laboratory operations that are subject to quality control. Each is treated in detail in later sections of this chapter.

In the discussion that follows it is assumed that methods have been standardized; analytical methods approved by EPA should be used whenever possible.

Techniques for controlling the major sources of analytical variability are presented in this chapter, along with the criteria for choosing the techniques best suited to a specific laboratory situation. Certain general criteria are applicable in nearly all laboratory applications; e.g., cost, requirements of the analytical methods, experience of other laboratories, and effects of interferences as determined through sensitivity testing.

5.2 Controlling Physical Parameters

5.2.1 Laboratory Support Services

Laboratory support services include laboratory gases, water, and electricity. The parameters that affect the quality of laboratory support services are given in Table 5.1 with suggested control techniques.

Decisions concerning the frequency with which generating and storage equipment should be maintained and reagents checked need to be made. Manufacturers' recommendations provide a reasonable starting point, but schedules can be adjusted as experience dictates. Initially, checks should be made more frequently than is recommended to provide data for decisions on scheduling. Maintenance contracts with the manufacturer provide a convenient, and often economically justified, method of meeting maintenance requirements.[16] When a laboratory reagent such as water or air has been purchased commercially, it should be subject to procedures, like conductivity tests for water, that will verify manufacturers' quality statements and verify that the reagent is not changing over a period of time in the laboratory. The results of all verification procedures should be

TABLE 5.1 TECHNIQUES FOR QUALITY CONTROL OF LABORATORY SUPPORT SERVICES

Support Service	Parameters Affecting Quality	Control Techniques
Laboratory Gases	Purity specifications - vary among manufacturers	Develop purchasing guides
	Variation between lots	Overlap use of old and new cylinders
	Atmospheric interferences	Adopt filtering and drying procedures
Reagent Water	Commercial source variation	Develop purchasing guides - Batch test for conductivity
	Purity requirements	Redistillation, heating, deionization with ion exchange columns
	Atmospheric interferences	Filtration of exchange air
	Generation and storage equipment	Maintenance schedules from manufacturer recommendations
Electrical Service	Voltage fluctuations	Battery power
		Constant voltage transformers
		Separate lines
		Motor generator sets
Ambient Conditions	Temperature	Heating and air conditioning systems
	Humidity	Humidity controls

recorded on standard format check sheets, which could include the following data:

- Date of receipt of container
- Container identification
- Manufacturer identification
- Lot number, if available
- Date of verification test
- Name and purpose of test
- Results of test
- Signature of the analyst

Procedural guidelines for purchasing laboratory gases and water can be developed by compiling definitions for purity specifications used by different manufacturers. Purchasing personnel should refer to such information to avoid confusion when they are attempting to maintain a constant quality of reagent, but must purchase from different manufacturers.

Procedures for testing the quality of support media should be developed with the aid of professional publications and manufacturers' literature. References 17 through 22 will be useful in designing procedures for testing quality of laboratory water and gases.

Considering the final application of the data generated will help in the decision of which control techniques to apply. The cost and effort required for some control techniques may not be justified in terms of the purpose of the analyses. If the data are used for internal preliminary survey work, for example, to determine the relative efficiency of a combustion process, control measures may be considerably less important than they would be if the data were used for setting emissions standards.

5.2.2 Chemicals and Reagents

A laboratory quality control program should include standard procedures for choosing chemicals, preparing standard solutions, storing and handling chemicals and reagents, and choosing and handling standard reference materials. Some of the parameters affecting each procedure are listed in Table 5.2 with some appropriate control techniques.

The control techniques for choosing chemicals include the development of purchasing guidelines. These guidelines should clarify the difference in grade designations used by various manufacturers. The American Chemical Society classifications can serve as the reference for most definitions.

Standard solutions may require occasional restandardization. If the analytical method does not indicate the required frequency of restandardization, the frequency can be established by considering any or all of the following criteria:

- Normality of the solution
- Frequency of exposure to the atmosphere
- Availability of inert storage containers
- Availability of storage that prevents temperature and light effects

- Cost of restandardization as opposed to making a new solution - depends on frequency of use

TABLE 5.2

GUIDELINES FOR QUALITY CONTROL OF CHEMICALS AND REAGENTS

Procedure	Control Parameter	Control Technique
Choice of Chemicals	Manufacturer designations Method purity specs.	Develop purchasing guides Use American Chemical Society designations as a base Develop purification or treatment procedures specified by method
Preparation of Standard Solutions	Calibrated glassware Standard reference materials (SRM) Stability	Purchasing guidelines Schedules for restandardization of solutions
Storage and Handling	Container composition Filtering or pretreatment Environmental sensitivity	Design a labeling system Purchase single lot numbers Rotate stock Control temperature, light, atmospheric exposure
Standard Reference Materials	Availability Stability	Store in temperature controlled atmosphere Desiccate when necessary Replace if instability is suspected Weigh to determine loss or degradation

Storage and restandardization requirements for several standard solutions as shown in Table 5.3.[8]

TABLE 5.3

RESTANDARDIZATION REQUIREMENTS

Solution		Storage Requirements	Frequency of Restandardization
0.02-1.0N	Sodium Hydroxide	Polyolefin	Monthly
0.02-1.0N	Hydrochloric Acid	Glass	Monthly
0.02-1.0N	Sulfuric Acid	Glass	Monthly
0.1N	Iodine	Amber Glass Refrigerate	Open Bottles-Weekly Sealed Bottles-Monthly
0.1N	Sodium Thiosulfate	Glass	Weekly
0.1N	Ammonium Thiocyanate	Glass	Monthly
0.1N	Potassium Dichromate	Glass	Monthly
0.1N	Silver Nitrate	Amber Glass	Monthly
0.1N	Potassium Permanganate	Amber Glass	Weekly

Storage and handling procedures for chemicals and reagents should include the use of a labeling system. Labels on chemical bottles should include the following:

° Chemical Name
° Formula
° Manufacturer
° Lot Number
° Date Received
° Expiration Date

Labels on standard solution bottles should include the following:

- Chemicals used
- Manufacturers
- Lot numbers
- Date of Preparation
- Date of next standardization
- Standardization data
- Analyst identification
- Conditions of analysis (temperature, pressure, humidity)

Standard reference materials are available from the National Bureau of Standards and from commercial manufacturers. They are used for standardizing solutions, calibrating equipment, and monitoring accuracy and precision of analytical technique. NBS classifies chemical standards as (1) primary standards, (2) working standards, and (3) secondary standards, having the following definitions:[22]

Primary Standard - A primary standard is a commercially available substance of purity 100 ± 0.02% accuracy

Working Standard - A working standard is a commercially available substance of purity 100 ± 0.05% accuracy

Secondary Standard - A secondary standard is a substance of lower purity that can be standardized against a primary grade standard

The availability of primary standards may be limited. Since analytical results rely on the accuracy of solutions made with standard reference materials, it is important that steps be taken in the laboratory to eliminate errors due to mishandling of standard reference materials. This is best accomplished by providing the analysts with written procedures for handling of standard reference materials. The vendors usually recommend storage and handling procedures (see Table 5.2).

5.2.3 Instruments

Standard procedures for operation, calibration, and maintenance of analytical instruments are important for interpreting results as well as for preventing errors. Table 5.4 shows the important control parameters for analytical instruments and the control techniques that apply to those parameters.

Function checks can be used to indicate whether a subsystem within an instrument is functioning properly within predefined limits. The limits are usually defined by the instrument manufacturer, and the user should determine whether the limits are acceptable for his requirements. The frequency with which function checks are performed depends on how the instrument is used. If the instrument is used for short periods each week, function checks may be performed with each use or even monthly. If the instrument is operated daily, function checks may be made daily or before each run.

The following example illustrates a function check of linearity of a spectrophotometer.

- Prepare a standard data sheet to record relative concentration of standards, readings at various wavelengths, date of test, analyst identification, remarks.
- Prepare four standard solutions that absorb strongly at selected wavelengths in the range of the analytical methods. Commercially prepared solutions were used for this example.

TABLE 5.4

TECHNIQUES FOR QUALITY CONTROL OF ANALYTICAL INSTRUMENTS

Control Parameter	Control Technique
Instrument Operating Range	Coordinate instrument selection with method requirements.
Interferences	Sample conditioning (drying, separating, mixing, etc.)
	Use of blanks
	Use of spiked samples
Environmental Conditions	Monitor and control temperature, humidity, pressure, any atmospheric parameter that can affect system response. Consult manufacturer instructions and method descriptions.
Associated Equipment (cuvettes, volumetric ware, dilutors, etc.)	Proper handling procedures
	Standard procedures for cleaning
	Standardization or calibration
Normal System Drift	Zero adjust
System Component Functions	Apply function tests
	Plot response to changing concentrations
	Perform maintenance when indicated
Response Readout	Use calibration curve, adjust using blanks and zero - span controls

- For each relative concentration, record the absorbance at the specified wavelengths.
- Using Cartesian graph paper (rectangular coordinates) plot a graph of absorbance vs. relative concentration. Prepare a separate graph for each wavelength. The graph should be a straight line if the instrument is functioning properly and if the absorbing solution follows Beer's Law.
- At each successive testing interval, plot the points as above.
- If the points for a wavelength appear to be on a straight line or to be equally distributed around it, the operator can assume that the instrument is functioning satisfactorily.
- If the points for a wavelength begin to fall consistently above or below the baseline and the distance between the points and the baseline increases, the operator should expect an impending problem that will require maintenance.

For the data obtained at 420 nm (Figure 5.1), the graph (Figure 5.2) indicates that the response is beginning to change. The manufacturer's literature should indicate whether the amount of drift is acceptable. If the drift is not within defined tolerance limits, maintenance should be performed according to manufacturer's recommendations.

Calibration provides a technique for translating instrument response into meaningful concentration units. A calibration curve is constructed by analysis of materials containing varying known concentrations of the element or compound of interest. Each time a curve is constructed, a test is applied to determine whether instrument response is within predefined limits. If the calibration curve is acceptable, i.e., if it lies within the statistical limits, then the analyst can apply it to translate instrument output

SPECTROPHOTOMETER WEEKLY FUNCTION CHECK

FOR LINEARITY AND PRECISION

Relative Concentration	ABS at 670 mu	ABS at 520 mu	ABS at 420 mu	Date	Analyst	Remarks
1.00	0.700	0.720	0.630	11-13	LAE	
0.75	0.525	0.535	0.480	↓	↓	
0.50	0.350	0.360	0.318			
0.25	0.175	0.180	0.165			
0.00	0.00	0.00	0.00			
1.00	0.700	0.720	0.625	11-20	LAE	
0.75	0.520	0.535	0.475	↓	↓	
0.50	0.345	0.360	0.315			
0.25	0.175	0.185	0.170			
0.00	0.00	0.00	0.00			
1.00	0.693	0.710	0.620	11-29	LAE	
0.75	0.517	0.530	0.465	↓	↓	
0.50	0.344	0.350	0.315			
0.25	0.175	0.175	0.162			
0.00	0.000	0.000	0.000			
1.00	0.708	0.720	0.618	12-4	LAE	
0.75	0.530	0.540	0.461	↓	↓	
0.50	0.350	0.350	0.313			
0.25	0.178	0.179	0.159			
0.00	0.00	0.00	0.00			
1.00						
0.75						
0.50						
0.25						
0.00						

Figure 5.1 Spectrophotometer weekly function check for linearity and precision

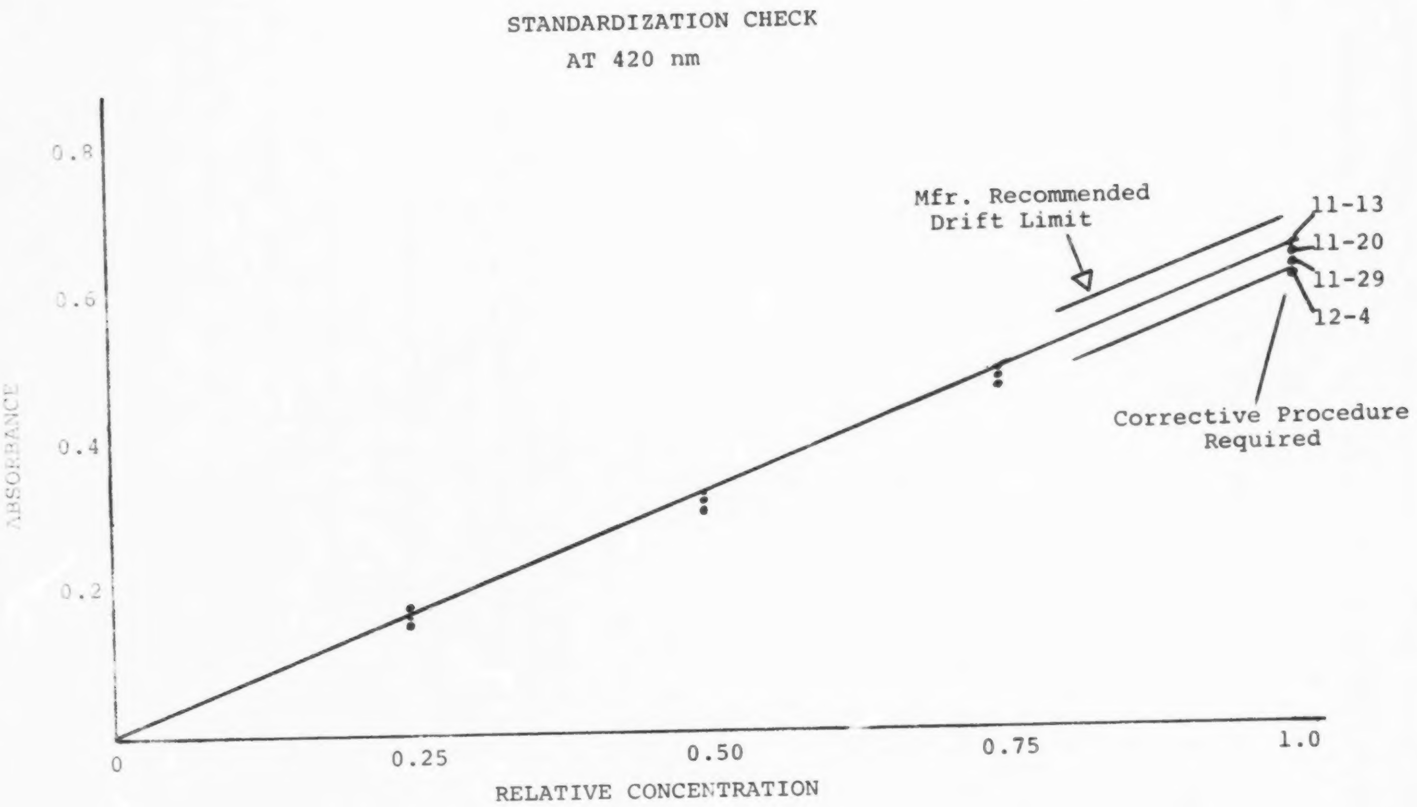


Figure 5.2 Standardization check at 420 nm

into the appropriate concentration units. The example for constructing an SO_2 calibration curve, presented in Appendix C, will show how to establish control limits.

The standards used to construct the calibration curve can be primary or working standards, or spiked standards designed to eliminate the effects of interferences encountered in real tests. In calibration the standard is exposed to the same preparatory steps that are applied to unknown samples. For example, if samples are subjected to a separation procedure, then the standard should also be subjected to that procedure. With this technique the analyst can introduce the same net interferences, as closely as possible, that will occur in normal application of the analytical methods. The choice of standard will depend on several criteria:

- Method requirements
- Expected concentration range of unknown samples
- Known interferences determined by method standardization and sensitivity tests
- Availability of standard reference materials
- Cost of standard reference materials
- Stability of standards

Many laboratories use a non-statistical approach to constructing calibration curves. The concentrations of the standard that are analyzed to provide data for calibration curves should cover the working range of the method. The data in Table 5.5 were used for constructing the calibration curve (Figure 5.3) for SO_2 determination using the modified pararosaniline method.

TABLE 5.5

SO_2 CALIBRATION DATA

Concentration	Average Absorbance
0.20	0.095
0.40	0.240
0.60	0.315
0.80	0.440
1.00	0.565
1.20	0.660
1.40	0.780

The steps used to construct the curve are:

- Analyze at least three concentrations of the standard. The concentrations should cover the working range of the method. Three replicates should be analyzed for each concentration.

- Plot the average absorbance values (y-axis) for each set of replicates against the concentrations (x-axis) on rectangular coordinate graph paper. If percent transmittance is plotted, semi-log graph paper should be used.

- Establish a calibration line by drawing a line of best fit through the plotted points. This line will not necessarily pass through the origin of the graph. The y-intercept can vary depending on such variable parameters as equipment sensitivity, environmental influences, or degradation of the standard.

Since the line of best fit can shift, the analyst should periodically analyze the standard at one of the concentration levels used to construct the calibration curve. The result can be plotted on the curve to indicate the

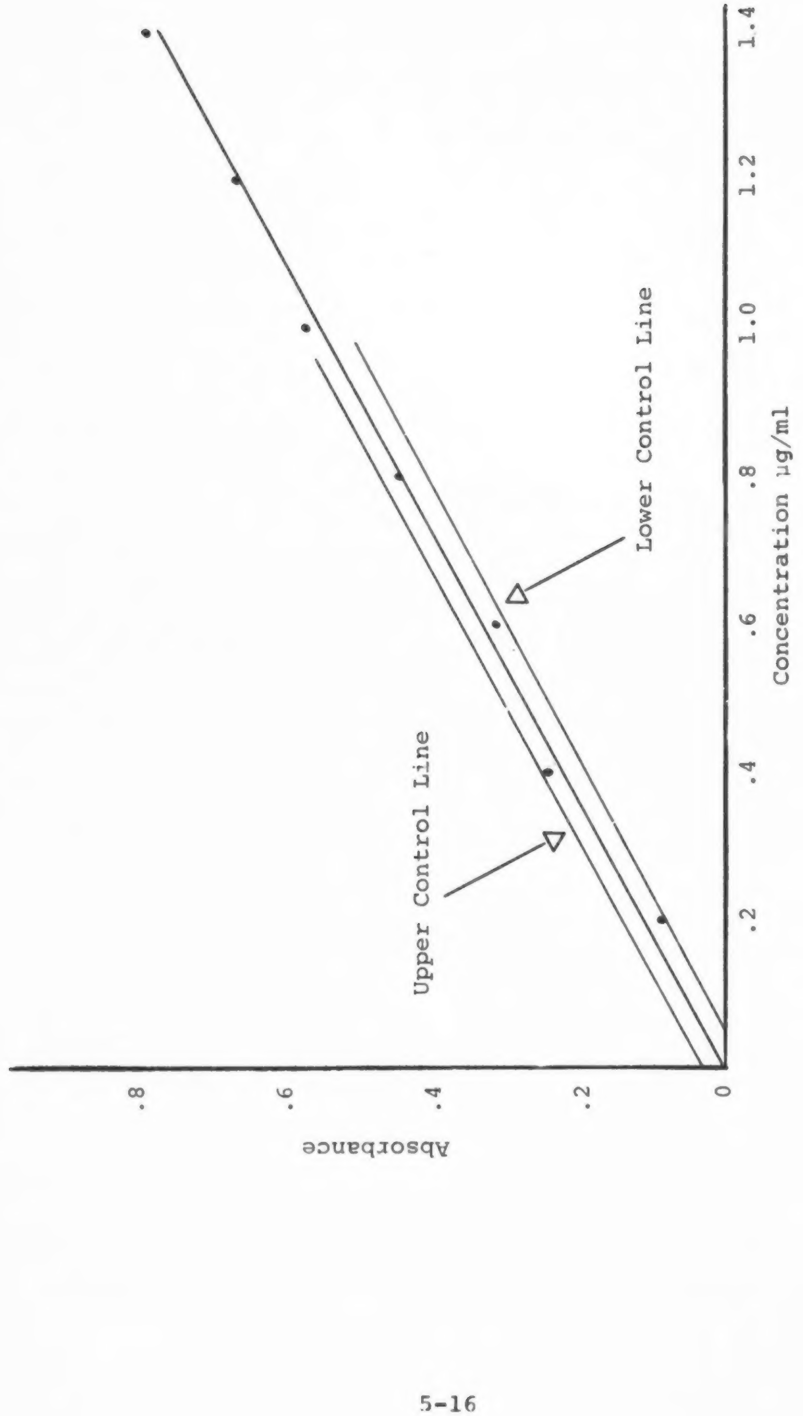


Figure 5.3 Calibration Curve for SO_2 Determination

degree of curve shift, if any. The frequency with which the curve should be checked depends on the reproducibility of the instrument, the ruggedness of the method, and changes in environmental influences. Control lines cannot be rigorously determined with statistical techniques for the type of calibration curve in this example. The control lines in Figure 5.3 merely illustrate that limits can be placed on the calibration curve if the method description specifies the limits. Each time the standard is analyzed, the result should lie within the established control lines. If it lies outside the control lines, a change in one or several parameters in the analytical system has occurred, and either corrective action or a new calibration curve is necessary. The technique just described is useful when the analytical method is to be used infrequently. However, when a method is being used routinely, the preferred technique for constructing the curve and its limits is regression analysis by the method of least squares.

To obtain maximum precision in determining the line of best fit, the EPA suggests in the Federal Register using regression analysis by the method of least squares. If this technique is used, statistical control limits for the calibration curve can be established that relate to different confidence intervals. We suggest that if an analytical method that requires a calibration curve is used continuously in the laboratory, regression analysis by the method of least squares is a better technique for constructing the calibration curves than is the previously explained technique. An example of how this statistical technique is applied appears in Appendix C.

5.2.4 Analytical Technique

The quality of analytical technique is a function of the analyst's experience and training. Basic operations, such as dilution procedures and handling of analytical weights, contribute significantly to indeterminate errors, i.e., errors that cannot be traced.

Maintaining good analytical technique in the laboratory is primarily a management task.[23] The laboratory supervisor can use several methods to encourage good technique and to insure a continuing effort to maintain good technique.

- Proper allocation of manpower
- Periodic review of analyst performance
- Implementation of maintenance schedules and procedures for all laboratory instruments and materials
- Design and review of error histories

If he is applying one or all of these methods to maintain good technique among the analysts, the supervisor can use a form of statistical analysis to evaluate and compare the performances. A control chart can be constructed for each analyst to show the variability of results he obtains with any given analytical method. Data used for such charts are from analysis of replicate samples or of known standards over a specified period of time. The analyst's performance can be compared with his performance over another time period to show trends in his proficiency, or it can be compared with the performances of other analysts using the same analytical methods.

The major problems with designing a program to monitor the analyst's performance are concerned with design of the sampling system. The problems are:

- What kinds of samples to use.
- How to prepare and introduce samples into the run without the analyst's knowledge.
- How often to check the analyst's proficiency.

The problems and their suggested solutions or criteria for decision are given in Table 5.6.

TABLE 5.6

PROBLEMS IN ASSESSING ANALYST PERFORMANCE

Problem	Solutions and Decision Criteria
Kinds of Samples	Replicate samples of unknowns or reference standards. Consider cost of samples. Samples must be exposed by the analyst to same preparatory steps as are normal unknown samples.
Introducing the Sample	Samples should have same labels and appearance as unknowns. Because checking periods should not be obvious, supervisor and analyst should overlap the process of logging in samples. Supervisor can place knowns or replicates into the system occasionally. Save an aliquot from one day for analysis by another analyst. This technique can be used to detect bias.
Frequency of Checking Performance	Consider degree of automation. Consider total method precision. Consider analyst's training and attitude.

In this discussion of quality control in an analytical laboratory we have considered the four major sources of variation or error; that is

- the laboratory facilities
- the reagents and materials
- the instruments, and
- the analysts.

We have described some measures for quality control in each category. Now we turn to the second phase of quality control that is required for effective laboratory operations - the application of statistical techniques and other review and control practices that together constitute in-depth analysis of the total measurement system.

5.3 Statistical Methods

Statistical techniques provide a means of defining acceptable levels of analytical performance and determining whether those levels are being achieved and maintained. The major steps in developing a statistical evaluation system are:

- ° Defining the performance levels.
- ° Choosing the statistical techniques.
- ° Constructing control charts.

5.3.1 Defining Performance Levels

Before a system for evaluating analytical performance can be initiated, acceptable performance levels must be defined. Laboratories normally work in the 99% confidence interval (see Section 2.2.2 discussion of adjustment factors and confidence intervals). Statistical formulae can be applied to determine confidence limits. No formula can be applied to determine confidence level, but several practical criteria can affect the choice:

° Method specifications
° EPA recommendations
° Ultimate use of the data
° Method standardization precision and accuracy data
° Intralaboratory and interlaboratory test results

5.3.2 Choosing Statistical Techniques

Statistical techniques are applied to determine whether the errors associated with analytical data are within operational limits designated for the method. Precision control charts are prepared from results of replicate analyses and are used to monitor the degree of variability among laboratory results.

Precision control charts indicate the level of precision in two ways: (1) in the unit of measurement of the variable; (2) in percent. Precision in units is calculated in terms of range (R-Chart) or standard deviation (S-Chart). Precision as percent is calculated in terms of the coefficient of variation (CV-Chart), also referred to as relative standard deviation.

$$R = \text{Max} - \text{Min}$$

$$S = \sqrt{\frac{\Sigma(x-\bar{x})^2}{N-1}}$$

$$CV = \frac{S}{\bar{x}}(100)$$

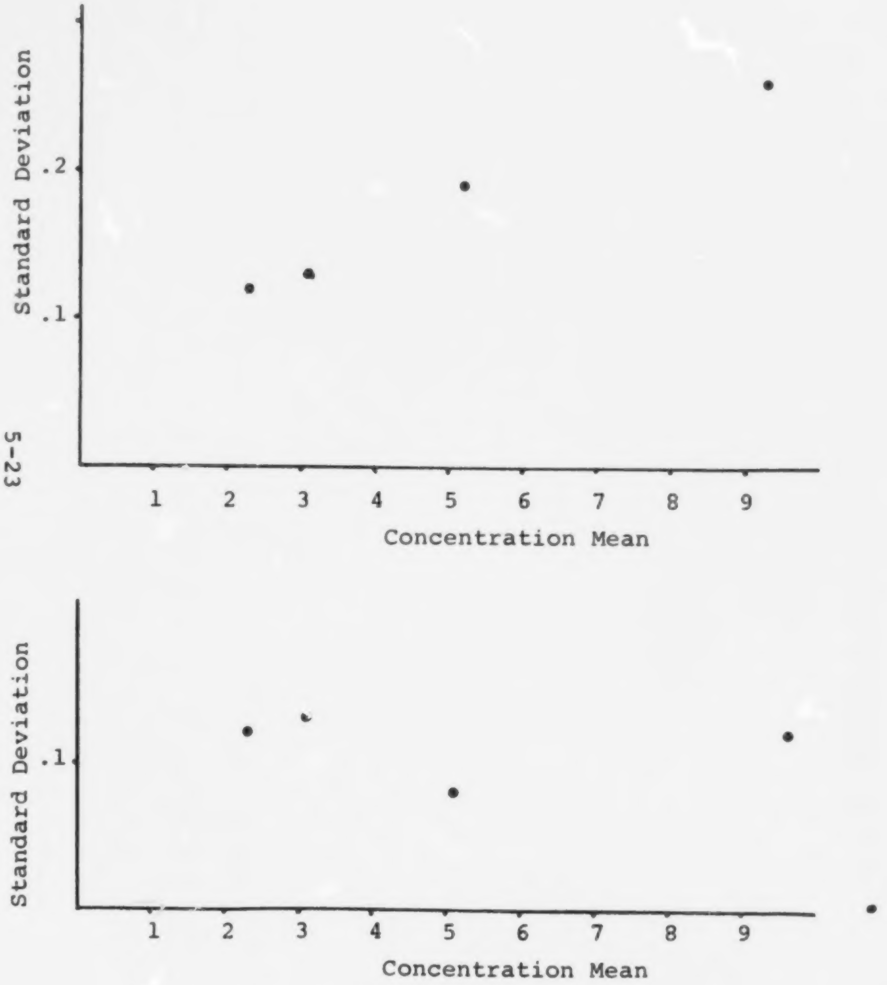
R = Range
S = Standard Deviation
CV = Coefficient of Variation
$\underline{x}$ = Individual Value
x = Mean Value
N = Number of Replicates

The use of R-Charts and S-Charts is based on the assumption of homogeneity of variance (i.e., the variation between replicate analyses on a single sample is constant over the range of concentration being measured). The CV-Chart is used when precision is dependent on the concentration being measured (i.e. the standard deviation changes, usually increasing, with concentration). The coefficient of variation, expressed as a percent, is independent of concentration from the standpoint that the percent is constant over the concentration range.

Before an analytical method is adopted for routine use in the laboratory, replicate analyses should be run on known standards. Prepare the standards to represent both the low and the high concentrations expected and at least one, but preferably two, intermediate concentrations. As a good "rule of thumb", between 5 and 10 replicate analyses should be run at each known concentration.

Compute the mean (x) and standard deviation (s_i) for each concentration. x_1 s_1, x_2 s_2, x_3 s_3, x_4 s_4. Plot the mean and standard deviation on a scatter diagram (Figure 5.4). Generally the scatter diagram will follow the pattern of one of the two cases shown.

Case A: The standard deviation is independent of the mean. Use either an R-Chart or S-Chart.



CASE B:

Standard Deviation
Increases with Concentration

CASE A:

Standard Deviation is
Independent of Concentration

Figure 5.4 Scatter Diagrams for Determining Control Charts

Case B: The standard deviation is dependent on changes in concentration. Use the CV-Chart.

Choice of an R-Chart or an S-Chart depends on the number of replicate analyses to be run routinely to monitor precision. If the number of replicates (n) is small ($n < 12$), the R-Chart is the most efficient. When n is large ($n > 12$) the S-Chart provides a more efficient control of precision. Since precision is usually determined on the basis of a small number of replicates, S-Charts for precision are not discussed in this manual. Table 5.7 presents data used to plot Case A and Case B in Figure 5.4.

5.3.3 Constructing Range Control Charts

The procedure for constructing a control chart for range follows (see Table 5.8):

- List the absolute value of the range (R) for each set of replicates.
- Compute the average range ($\bar{R}$) for all sets of replicates.
- Compute the upper control limit by $UCL = D_4\bar{R}$. D_4 is from Table BII, Appendix B.
- Compute the lower control limit by $LCL = D_3\bar{R}$. D_3 is from Table BII, Appendix B.
- Plot the line for R on the control chart.
- Plot the values for ranges of each set of replicates (Figure 5.5).

The control limits computed for this control chart are for the 99% confidence interval (see Section 2.2.2). Therefore 99% of the calculated range values should be between these control limits.

TABLE 5.7
DATA USED TO CONSTRUCT SCATTER DIAGRAMS

CASE A			CASE B		
x	$x-\bar{x}$	$(x-\bar{x})^2$	x	$x-\bar{x}$	$(x-\bar{x})^2$
2.3	0	0	2.3	0	0
2.2	-.1	.01	2.2	-.1	.01
2.3	0	0	2.3	0	0
2.4	1	.01	2.4	1	.01
2.1	-.2	.04	2.1	-.2	.04
$\bar{x}$ = 2.3		S = .12	$\bar{x}$ = 2.3		S = .12
3.0	-.1	.01	3.0	-.1	.01
3.1	0	0	3.1	0	0
3.2	.1	.01	3.2	.1	.01
2.9	-.2	.04	2.9	-.2	.04
3.2	.1	.01	3.2	.1	.01
$\bar{x}$ = 3.1		S = .13	$\bar{x}$ = 3.1		S = .13
5.1	0	0	5.1	-.1	.01
5.0	-.1	.01	5.2	0	0
5.2	.1	.01	5.4	.2	.04
5.1	0	0	4.9	-.3	.09
5.0	-.1	.01	5.3	.1	.01
$\bar{x}$ = 5.1		S = .08	$\bar{x}$ = 5.2		S = .19
9.5	-.1	.01	9.5	.2	.04
9.6	0	0	9.1	-.2	.04
9.4	-.2	.04	9.6	.3	.09
9,7	.1	.01	9.0	-.3	.09
9.6	0	0	9.2	-.1	.01
$\bar{x}$ = 9.6		S = .12	$\bar{x}$ = 9.3		S = .26

TABLE 5.8 COMPUTATION OF CONTROL LIMITS FOR RANGE CONTROL CHARTS

Sample (n)	x_1	x_2	R
1	21	29	8
2	39	47	8
3	14	18	4
4	8	10	2
5	59	71	12
6	88	96	8
7	7	9	2
8	88	98	10
9	38	46	8
10	22	28	6
		R Total =	68

$$\bar{R} = \frac{R}{n} = \frac{68}{10} = 6.8$$

$$UCL = D_4\ \bar{R} = 3.267 \times 6.8 = 22.22$$

$$LCL = D_3\ \bar{R} = 0 \times 6.8 = 0$$

D_3 and D_4 are for $n = 2$

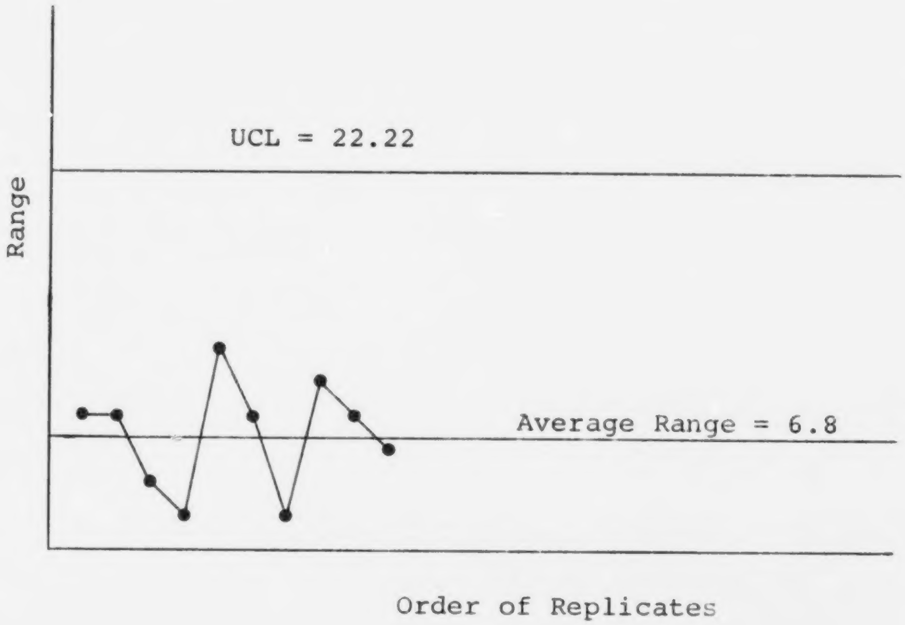


Figure 5.5 Control Chart for Range

Data plotted on precision control charts should be approximately evenly distributed around the mean value line. The Theory of Runs dictates that, for the 99% confidence level, if eight successive values appear on one side of the mean value line, then the process is judged to have bias. If this occurs, stop the process and follow a standard routine for error tracing to find the source of error that is causing the bias. Note the problem and the error source on the control chart for easy future reference. A system for tracing errors is described later in this chapter.

If any of the results plotted on the control chart fall outside of the control limits, the process should be judged out of control and the analysis stopped. Whenever possible, reanalyze all affected samples when a bias or an out-of-control situation is observed. The feasibility of identifying and reanalyzing affected samples depends on the frequency with which replicate samples are analyzed. For example, if few samples are analyzed by a method each day, and only one set of replicates is analyzed each day, bias would not be confirmed on the control chart until at least the end of eight consecutive days. It would be impractical, and in many cases impossible, to save an aliquot of each sample for at least eight days for the possibility of reruns. Keep in mind that biased results are still acceptable if the control limits are not exceeded. The most important step is to find the source of error and correct it before it causes the analytical process to go out of control.

Inspection of the control chart will help to determine which samples may have been affected if bias or loss of control occur. In a bias situation, all samples associated with the eight sets of replicates that produced the plotted control data can be considered to have been affected. This situation is illustrated by Case A in Figure 5.6. When loss of control is indicated, all samples analyzed between the last set of replicates that showed control and the set of replicates that indicated loss of control can be considered to have been affected (Case B, Figure 5.6). An exception to Case B would be the appearance of an upward or downward trend of the control data prior to loss of control (Case C, Figure 5.6). This could be a situation in which the analytical process was subject to bias but went out of control before enough replicates were analyzed to display the bias. In this case the control data points are traced back to the last point appearing on the side of the mean value line opposite the points that indicate suspected bias. All samples beyond this point could have been affected.

5.3.4 Constructing Coefficient of Variation Charts

The CV-Chart is prepared from measurements obtained from replicate analyses of routine samples. Typically the number of replicates is two. The duplicate analyses are

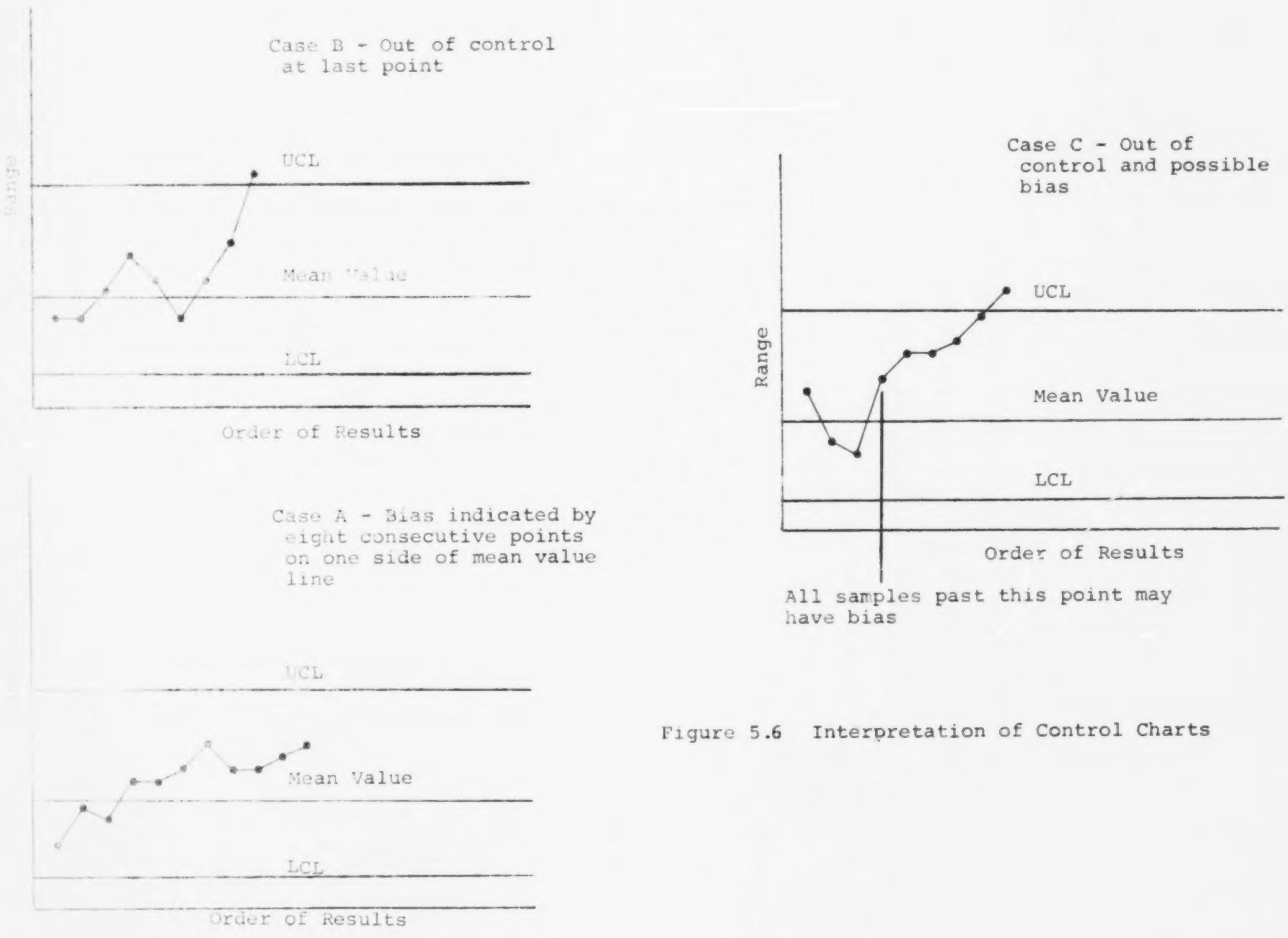


Figure 5.6 Interpretation of Control Charts

run on 5-10 percent of the incoming samples, selected by a random process. The duplicates are sent to the analyst in such a manner that the analyses are run "blind", i.e. the analyst cannot determine which samples are being used to monitor precision.

It is difficult to rigorously determine the number of duplicate analyses needed to establish the necessary control limits, but a minimum of 15-20 is preferred. Similarly, as the duplicate analyses yield more data, control limits should be revised periodically, perhaps monthly or quarterly. Cumulative data may indicate that control limits should be revised annually.

The procedure for constructing the CV-Chart for the data in Table 5.9 is described below. The term "sample"

TABLE 5.9 COMPUTATION OF CONTROL LIMITS FOR CV-CHART

Sample	x_1	x_2	R	$\bar{x}$	CV
1	23	29	6	26	16.3
2	39	47	8	43	13.2
3	14	18	4	16	17.7
4	8	10	2	9	15.7
5	59	71	12	65	13.0
6	78	96	18	87	14.6
7	7	9	2	8	17.7
8	80	98	18	89	14.3
9	38	46	8	42	13.5
10	22	28	6	25	17.0
11	12	16	4	14	20.2
12	29	35	6	32	13.3
13	48	60	12	54	15.7
14	75	91	16	83	13.6
15	48	58	10	53	13.3
16	80	100	20	90	15.7

Σ CV = 244.8

refers to a set of duplicates. The range is used here for convenience, since it is an efficient estimate of standard deviation for $n = 2$.

- Compute the range R for each sample.
- Compute the arithmetic mean $\bar{x}$ for each sample.
- Compute the coefficient of variation for each sample, where:

$$CV = \frac{R}{\bar{x}\sqrt{n}}$$

n = sample size 2

- Compute the average coefficient of variation.

$$\overline{CV} = \frac{\sum_{1}^{16} CVi}{16} = \frac{244.8}{16} = 15.3$$

- Compute the upper control limit.

$$UCL = B_4 \overline{CV}$$

where $B_4 = 1.552$ (Table BIII, Appendix B) for $n = 16$

$$UCL = 1.552 (15.3) = 23.75$$

- Compute the lower control limit.

$$LCL = B_3 \overline{CV}$$

where $B_3 = 0.448$ for $n = 16$

$$LCL = 0.448 (15.3) = 6.85$$

- Prepare the CV-Chart (Figure 5.7) showing $\overline{CV}$, UCL, and LCL.

The CV-Chart is now ready for use to monitor precision of routine sample analysis. For each sample compute CV and plot new values sequentially on the control chart.

5.3.5 Determining Accuracy

Accuracy determinations involve the comparison of results from analysis of unknown samples with results from

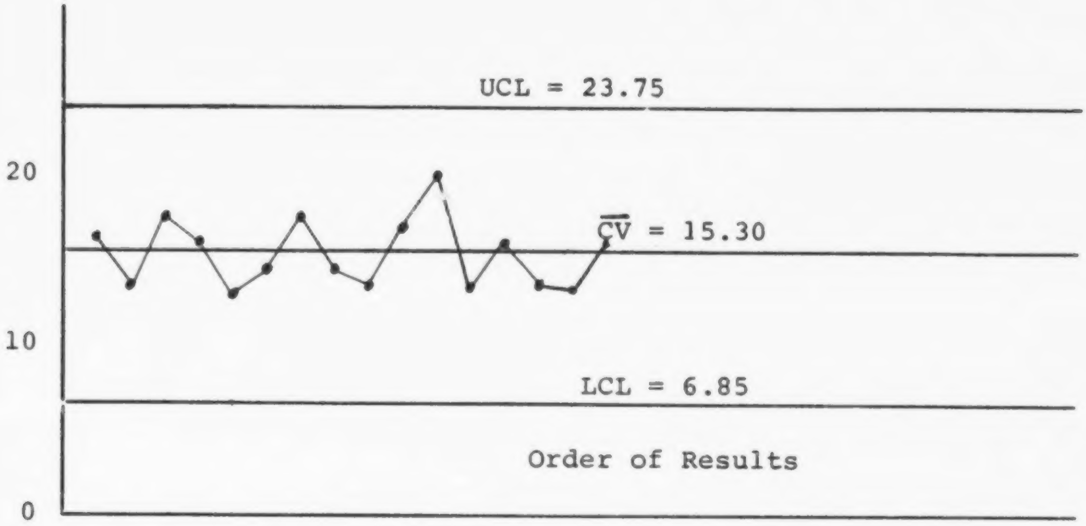


Figure 5.7 Coefficient of Variation Chart

analysis of standards of known concentration. Two techniques for accuracy determination, classified by type of reference material, are shown in Table 5.10 with the criteria that affect the choice of each.

One problem with using a primary or a working standard for accuracy determination is that these standards do not approximate the quality of actual samples. Field samples are exposed to a variety of sources of interference during their collection and transport to the laboratory. After arrival at the laboratory, the samples are subjected to more potential sources of interference during sample preparation. The effects of those interferences are significant for many

TABLE 5.10 TECHNIQUES FOR DETERMINING ACCURACY

Analytical Technique	Criteria for Application
Pure standards	Often not available. Advantage - composition is well established. Disadvantage - does not duplicate the sample. Interferences normally found in samples are not present, and effect on method cannot be measured.
Spiked samples Standard addition (% recovery technique)	Can be used when stable standards cannot be obtained. Can be used when accuracy determinations are very infrequent. Applicable for trace analysis.

types of analyses, such as atomic absorption analysis for trace metals. Consequently, when accuracy is being determined it is often desirable to compensate for the net effects of normal interferences. The standard additions technique does this by providing a correction factor that can be applied to observed values to calculate true values for the analytical results.

A method of standard additions using only one addition is commonly called spiking and includes the following steps:[24]

- Analyze an aliquot of the unknown sample.
- Add to another aliquot of sample a portion of a standard of the species of interest such that the total concentration of the resulting solution will be within the optimum detection range of the method. Analyze the resultant mixture.
- Calculate the recovery of the added substance with the following formula:

$$\frac{C(s + a)}{Ca + Cs} \times 100 = \%\ \text{Recovery}$$

where: $C(s + a)$ = Observed concentration value of sample plus standard

Cs = Observed concentration value of sample

Ca = Actual value of standard

The percent recovery represents a correction factor for interferences, and the true value of a sample concentration is calculated by dividing the observed value by the percent recovery. This is true, however, only under limited circumstances (linearity of response). Merely adding a spike can introduce nonlinearity by volume change if that change is large enough to shift an equilibrium. Spiking materials can conceivably introduce unsuspected chemical nonlinearities also.

Improved results can be obtained by using a series of standard additions. Normally additions which are equal to twice and one-half of the original amount are optimum. The resulting readings are plotted against the concentration of the increments of the standard solutions that were added to the unknown. The extrapolated line intersecting the mirror image of the concentration response axis indicates the amount of unknowns in the sample (Figure 5.8).

The method of standard addition is well established as an evaluation method. By its use a number of interferences can be overcome; it is particularly suited for residual matrix effects and in trace analysis. However, limitations exist which must be

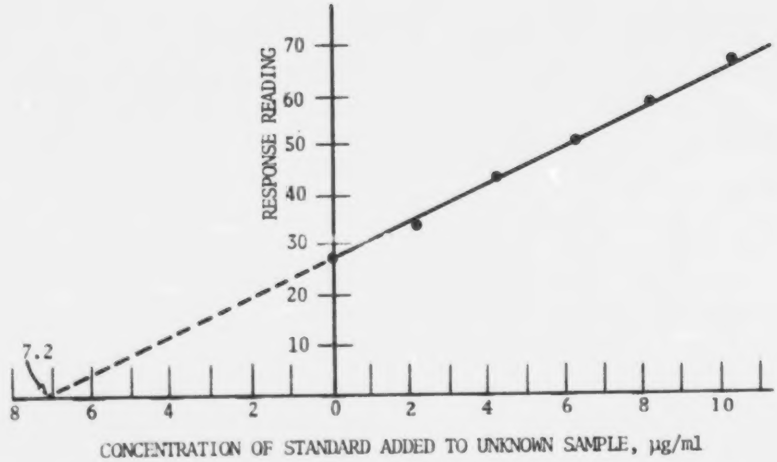


Figure 5.8. Graphical representation of the standard-addition method of evaluation.

recognized. The calibration curve must be linear over the range of concentrations employed and it must pass through the origin. It is desirable that all the solutions be diluted to the same final volume, for then any interfering substance will be present at the same concentration in all solutions.

5.3.6 Control Charts for Accuracy

Control charts on which to plot the results from accuracy determinations can be constructed in much the same manner as precision control charts. Standard deviation is convenient for measuring the variability among the accuracy determination results. Two situations are discussed in this section: (1) a primary or working standard is analyzed to determine accuracy; (2) the method of standard additions is used to determine accuracy.

Figure 5.9 illustrates the first situation, in which percent nitrogen has been determined by titration. Table 5.11 presents the data used. The control chart in Figure 5.9 was constructed by the following steps:

- Analyze 15-20 aliquots of a primary standard over a period of time sufficient to insure that normal laboratory operating conditions are represented. Compute the mean percent nitrogen value for all analyses. This value will represent the nominal value about which analytical values from later tests will be plotted. Do not be confused by the expression of nitrogen concentration as a percent. This is not a percent recovery technique.
- Calculate the standard deviation by:

$$S = \sqrt{\frac{\Sigma (x - \bar{x})^2}{n - 1}}$$

- Calculate a lower and upper control limit by:

$$UCL = \bar{x} + D_4 S$$

and $LCL = \bar{x} - D_4 S$

Use $D_4 = 1.652$ for the 99% confidence level, when $n = 15$

- Construct the chart.
- The formula for computing standard deviation in this example is interchangeable with the formula in the next example.

In the second example percent recovery is used to determine accuracy. In the percent recovery technique the control chart represents recovery efficiency, whereas in the technique just described the control chart represented analytical values. In preparing a control chart for percent recovery, follow these steps:

TABLE 5.11 ACCURACY DATA FOR PERCENT NITROGEN

Sample	% Nitrogen (x)	$x - \bar{x}$
1	25.89	.17
2	25.92	.20
3	25.87	.15
4	25.83	.11
5	25.79	.07
6	25.53	-.19
7	25.39	-.33
8	26.00	.28
9	25.53	-.19
10	25.90	.18
11	25.83	.11
12	25.60	-.12
13	25.65	-.07
14	25.80	.08
15	25.40	-.32

$\underline{S} = 0.207$
$\bar{x} = 25.72$

$D_4\ S = 1.652\ (0.207)$
$= .342$

$UCL = 25.72 + .342$
$= 26.06$

$LCL = 25.72 - .342$
$= 25.38$

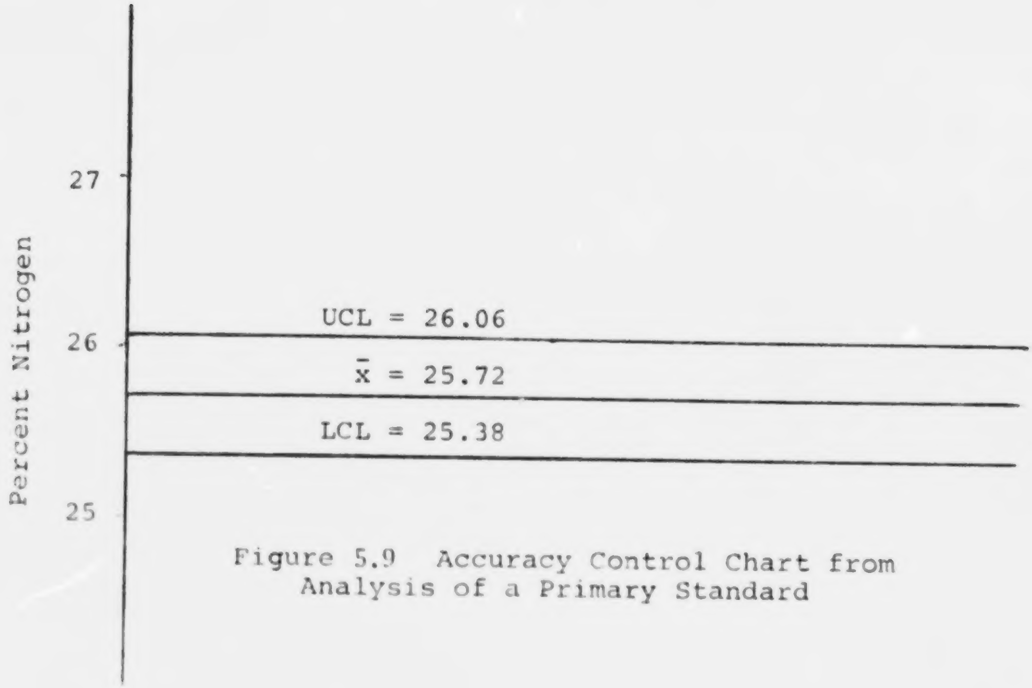


Figure 5.9 Accuracy Control Chart from Analysis of a Primary Standard

- Perform the recovery procedure 15-20 times and use the results for calculations.
- Calculate the average ($\bar{x}$) for all percent recoveries. The average will become the mean nominal value for the control chart.
- Compute the standard deviation of the percent recoveries by:

$$S = \sqrt{\frac{n\ \Sigma x^2 - (\Sigma x)^2}{n(n - 1)}}$$

Convenience determines which formula to use for standard deviation.

- Compute the upper control limit and the lower control limit by UCL = $\bar{x} + D_4\ S$ and LCL = $\bar{x} - D_4\ S$. D_4, as it was in the previous example, is based on $n = 15$.
- Plot the mean value for all the recoveries on the control chart and construct the upper and lower control limits. The control chart is now ready for plotting percent recovery data as generated. Table 5.12 shows the data used to construct Figure 5.10..

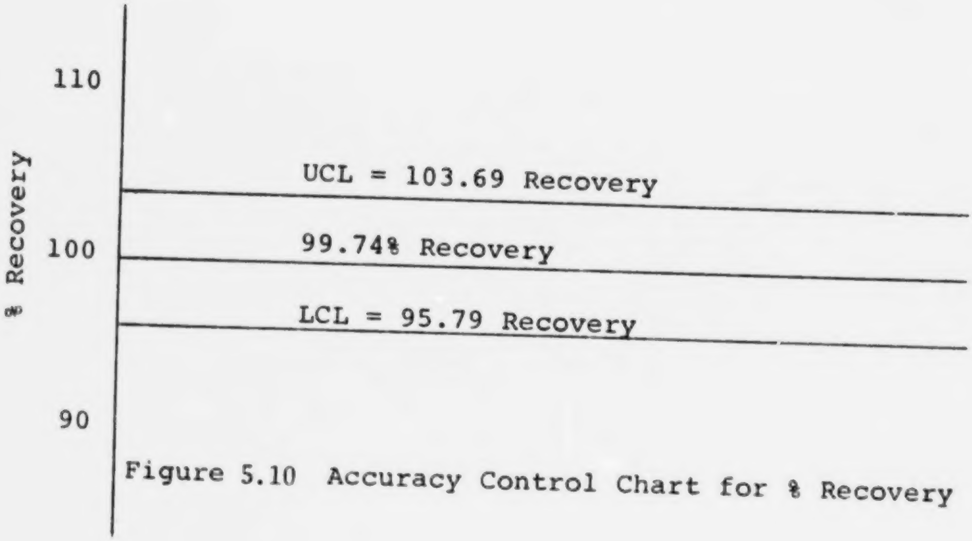


Figure 5.10 Accuracy Control Chart for % Recovery

TABLE 5.12 PERCENT RECOVERY DATA

Sample	% Recovery x
1	.982
2	.990
3	.993
4	1.005
5	1.021
6	1.030
7	.970
8	.975
9	.985
10	.998
11	1.011
12	1.020
13	1.015
14	.986
15	.980

$\Sigma x^2 = 14.93$

$D_4 = 1.652$ for $n = 15$

$\bar{x} = .9974$

$S = .0239$

$$\begin{aligned} UCL &= \bar{x} + D_4 S \\ &= .9974 + 1.652\,(.0239) = 1.0369 \\ &= 103.69\% \end{aligned}$$

$$\begin{aligned} LCL &= \bar{x} - D_4 S \\ &= .9974 - 1.652\,(.0239) \\ &= .9579 = 95.79\% \end{aligned}$$

The control chart constructed from the data in Table 5.12 has the mean nominal value line at the point representing the 99.74% recovery level. The upper control limit represents the 103.69% recovery level, and the lower control limit represents the 95.79% recovery level. Perfect recovery would be at the 100% level. Negative interferences would be expected to keep the recovery below 100%, but positive interferences can also influence an analysis. The positive interferences are stronger than the negative when the percent recovery is found to be more than 100 percent. The direction of each percent recovery from the 100 percent level, then, can indicate the kinds of errors to look for when control limits are exceeded.

5.4 Interlaboratory Proficiency Testing

The purpose of an interlaboratory proficiency testing program is to determine the relative proficiency of a group of laboratories and/or analysts in performing an analytical method. Laboratories participating in such programs are provided with standard reference samples and instructions for analysis of those samples. A co-ordinating laboratory prepares the samples and evaluates the results. Participation in interlaboratory programs is recommended.

Several problems can occur in proficiency testing programs. Some are procedural or administrative problems, and some are technical problems related to method standardization and ruggedness testing.

How to obtain unbiased treatment of the sample is an important problem in proficiency testing programs. Samples that are analyzed as part of a proficiency testing program should be placed in the sample run as unknowns. If the analyst recognizes the sample as coming from the referee laboratory, he could use extra care in the analysis, and the result would not represent his normal proficiency with the method.

Stability of the sample is an important technical consideration. The referee laboratory should determine the net effect of storage and transportation on the sample. The Center for Disease Control, Atlanta, Georgia, has employed a technique called "pigeon sampling". A sample is prepared and an aliquot is analyzed. Another aliquot is shipped to a designated point and returned unopened to the central laboratory. The aliquot is analyzed, and the results are compared with those obtained for the sample aliquot before shipment. The difference is an indication of the net effect of transporting the sample.

Before a method can be used routinely to rate the proficiency of laboratories participating in the program, it must be subjected to extensive testing to determine the total effect of changes in operating parameters. Disagreement among analytical results from different laboratories can indicate that the laboratories are not controlling to the same extent the parameters that affect the final results.

A case study involves the disagreement in results from two laboratories using the SPADNS - Zirconium Lake Method for determination of fluorides in stack gas.[25] A statistical analysis indicated that the difference between the results of Laboratory A and Laboratory B was significant.

Because of the significance of the difference in analytical results, steps were initiated to determine any operational differences in the use of the method by the two laboratories. The investigation showed two major differences:

1) Laboratory B varied the steps of the method, but varied each step in the same manner each time;

2) Laboratory A stayed within the operational ranges for each parameter, but varied inconsistently within those ranges. The specific differences are shown in Table 5.13 below.

TABLE 5.13 VARIATIONS IN METHOD PROCEDURES

Method Description	Laboratory A	Laboratory B
Charge still with 0.5 to 0.9 mg fluoride	Same as method	Charge still with 0.4 to 0.6 mg fluoride
Perform determinations at 15° to 30°C	Same as method	Perform determinations at 24.8°C
Change $H_2SO_4 \cdot H_2O$ mixture when recovery check indicates necessity	Same as method	Change $H_2SO_4 \cdot H_2O$ mixture every three runs

A program was undertaken at Laboratory A to determine the effects of varying the parameters outlined in the method description. The investigation showed that change in the temperature parameter made a significant difference in the analytical results. The procedure follows:

- Data were obtained by using the method with temperature control (SPADNS (b)) and by using the method without temperature control (SPADNS (a)).
- Data were obtained by using the method with temperature control (SPADNS (b)) and by using a specific ion electrode (c).
- The differences in results between (a,b) and (b,c) were analyzed to determine significance.

Comparative data analysis gave the following results:

	SPADNS(a)-SPADNS(b)	SIE(c)-SPADNS(b)
No. of samples	18	18
Average difference	-0.79	-0.10
Standard deviation of difference	0.98	0.67
Student "t" value	-3.4 (Significant)	-0.66 (Not Significant)

NOTE: For a sample of size n = 18, if t = -0.66, the probability that the two methods yield similar results is about 0.50. However, if t = 3.4 the probability that the two methods yield similar results is less than 0.005. It is generally accepted that a probability of 0.05 or less is sufficient to allow one to conclude that the difference between the methods is statistically significant.

These data show that the temperature is more critical than was indicated in the initial method description. For use in interlaboratory proficiency testing, it is important that the operating parameters of the analytical method be specifically defined.

5.5 Tracing Errors

When precision or accuracy control charts indicate that the analytical process is in error, it is necessary to find the source of error and to correct it. The histories and records from calibration, function checking, maintenance, and material quality checks can provide information with which to trace the sources of analytical variability.

To make optimal use of time and resources when tracing an error, the analyst should perform the search in a standard logical pattern designed so that the most obvious sources of error are considered first. If the search must then progress to less obvious sources of error, the procedure becomes more involved. A review of reagent standardization charts may be required and perhaps such procedures as parallel analysis using the original standard solutions before and after restandardization, if the restandardization results differ.

Table 5.14 illustrates one classification of error-tracing procedures according to complexity.

TABLE 5.14 CLASSIFICATION OF ERROR SOURCES

Source of Error	Explanation	Input to Tracing Procedure
Variation of Method Steps (Intentional)	A procedure or material specified has been changed or substituted.	Control chart - look for trend on all samples. Method description.
Unintentional Method Variation	A procedure has been altered or deleted unintentionally.	Method description - note special requirements such as sample preparation.
Change in Sample	The sample has changed or an interference has been introduced.	Field sampling records. Sample label data.
Analytical Error	An error has occurred in a basic procedure such as dilution, scale reading, weighing, etc.	Calibration data for dilutors, volumetric ware, etc. Calibration curves. Maintenace logs. Function check results for instruments.
Change in Reagent or Materials	A change has occurred in a reagent or in a material selected to use in the preparation or storage of reagents or in preparation of sample.	Standardization and check lists for reagents and laboratory services. Method description - look for storage requirements, preparative steps.

The flow diagram, Figure 5.11, shows the steps that would be followed for the third level of complexity in error tracing. At this level the analyst suspects that interferences have been introduced into the sample during collection, storage or transport, or during sample conditioning and preparation in the laboratory. Pertinent input data are shown, and logical alternatives are suggested.

The specific classification of error sources and the logical steps involved in tracing the errors differ in each laboratory. Application of the error tracing technique depends on the methods used, complexity of the routine operational checking and maintenance procedures, and the training of the analysts and their understanding of the methods.

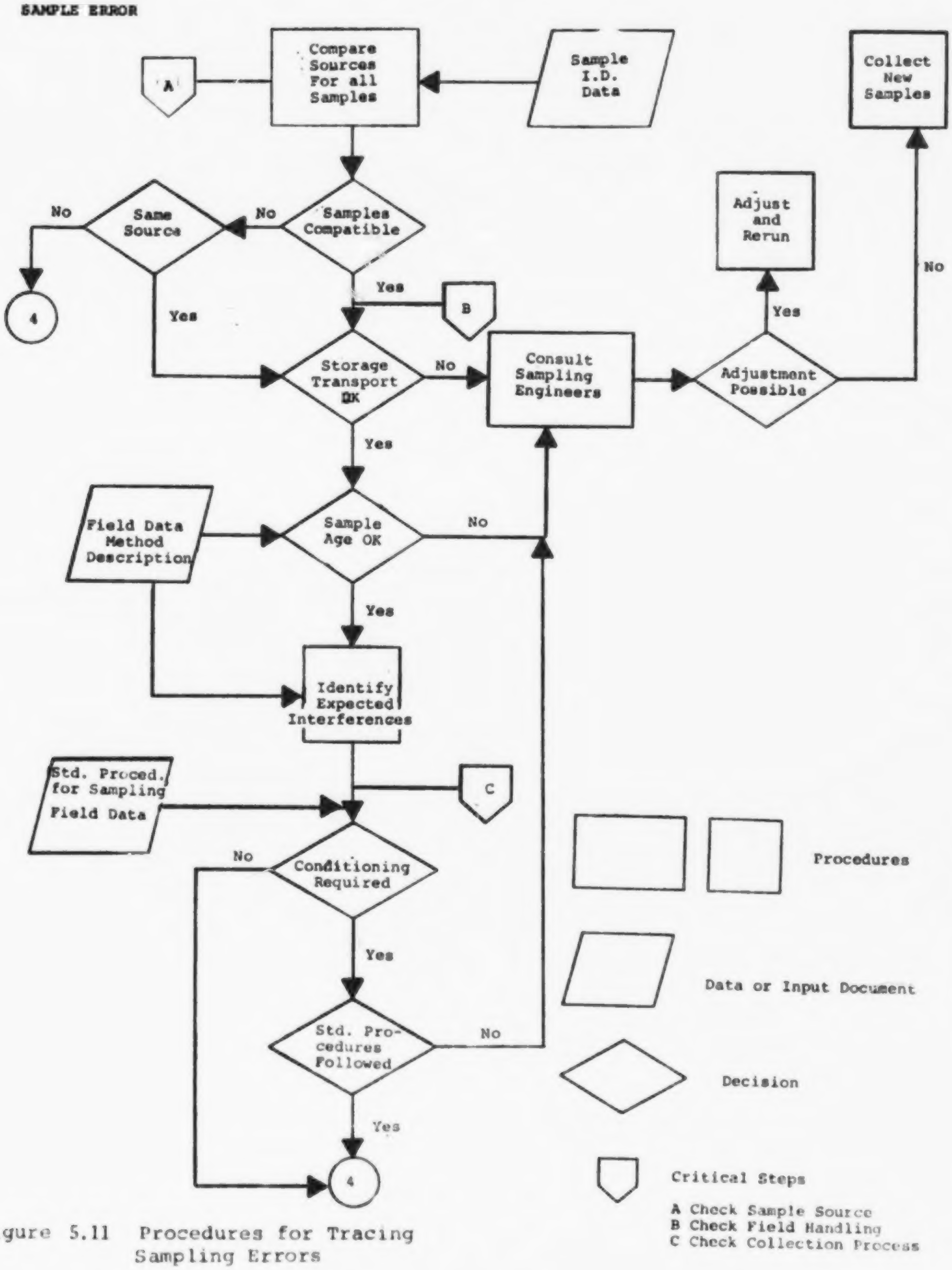

SAMPLE ERROR
A
Compare Sources For all Samples
Sample I.D. Data
Collect New Samples
No
Same Source
No
Samples Compatible
Adjust and Rerun
No
Yes
4
Yes
B
Yes
Storage Transport OK
No
Consult Sampling Engineers
Adjustment Possible
Yes
Field Data Method Description
Sample Age OK
No
Yes
Identify Expected Interferences
Std. Proced. for Sampling Field Data
C
No
Conditioning Required
Yes
Std. Procedures Followed
No
Yes
4
Procedures
Data or Input Document
Decision
Critical Steps
A Check Sample Source
B Check Field Handling
C Check Collection Process

Figure 5.11 Procedures for Tracing Sampling Errors

6.0 DATA HANDLING AND REPORTING

6.1 General

Measurements of the concentration of a contaminant, either in the ambient atmosphere or in the exhaust gas from an emission source, are assumed to be representative of the conditions existing at the time of sample collection. The extent to which this assumption is valid depends on the sources of error and bias inherent in the collection, handling and analysis of the sample. Methods that have been thoroughly researched and evaluated should have minimal error and no bias.

Besides the sampling and analytical error and bias, human error may be introduced anytime between sample collection and sample reporting. Included among the human errors are such things as failure of the technician to record pertinent information, mistakes in reading an instrument, mistakes in calculating results, mistakes in transposing data from one form to another. Data handling systems involving the use of computers are susceptible to keypunching errors and errors involving careless handling of magnetic tapes and other storage media. Although human error cannot be completely avoided, it can be minimized.

6.2 Data Recording

Methods for determining concentrations of air contaminants can be classified into two categories: (1) intermittent, (2) continuous. In most intermittent methods a discrete sample is collected in some media and is sent to a laboratory for the analytical determination. Both the field technician and the laboratory analyst can make errors in data handling. Continuous methods involve an analytical sensor that produces a direct readout of the pollutant concentration. The readout may be an analog record traced on a moving strip chart, or it may be a value punched on paper tape or written on magnetic tape. Some systems use telemetry to transmit data in real-time to a data processing facility.

6.2.1 Data Errors in Intermittent Sampling

The field technician records information before and after the sample collection period. This information includes identification of the sampling location, start and stop date and time, and data pertaining to flow rates, etc. It is necessary to rely on the integrity of the field personnel that such items as location, start and stop time and data are recorded correctly. Acceptability limits should be set for data pertaining to flow rates, etc., and the technician should invalidate the sampling data when values fall outside of these limits. Questionable measurement results indicate the need for instrument maintenance or calibration.

The analyst in the laboratory reads measurements from balances, colorimeters, spectrophotometers, and other instruments and records the data on standard forms or in laboratory notebooks. Each time he records a value he has the potential for incorrectly entering the result. Typical recording errors are transposition of digits (i.e. 216 could be incorrectly entered as 126) and incorrect decimal point location (i.e. .0635 could be entered as 0.635). These kinds of errors are difficult to detect. The laboratory director must continually stress the importance of accuracy in recording results.

6.2.2 Data Errors in Continuous Sampling

Continuous air monitoring systems may involve either manual or automated data recording. Manual data recording is used to reduce data from strip charts. Automated data recording may involve the use of a data logging device to record data on paper tape or magnetic tape at the remote sampling station, or the use of telemetry to transmit data on-line to a computer at a central facility.

Manual reduction of pollutant concentration data from strip charts can be a significant source of data errors. In addition to those errors associated with recording data values on record forms, the individual reading the chart can also err in the determination of the time-average value. Usually the reader estimates by inspection the average concentration. When the temporal variability in concentration is large, it is difficult to determine an average concentration. Two persons reading the same chart may yield results that vary considerably.

Individuals who will be responsible for reducing data from strip charts should be given extensive training. After a trainee is shown how to read a chart, his results should be compared with those of an experienced technician. Only after a technician has demonstrated that he is capable of obtaining satisfactory results should he be assigned to the data reduction activity.

Periodically the supervisor or senior technician should check strip charts read by each technician. When it becomes obvious that an individual is making gross errors it may be necessary to provide additional training.

Because manual chart reading is a tedious operation, a drop in productivity and reliability can be expected after a few hours. Ideally an individual should be required to spend only a portion of a day at this task.

The use of a data logging device to automate data handling from a continuous sensor is not a strict guarantee against data recording errors. Internal validity checking is necessary to avoid serious data recording errors. There are two sources of error between the sensor and the recording media: (1) the output signal from the sensor; (2) errors in recording by the data logger.

A system recently installed by the Division of Air Pollution Control, Cincinnati, Ohio, has validity checks for both sources of error. In this system a number of air quality and meteorological sensors are interrogated at 5-minute intervals. The data values are assembled into a record and written on magnetic tape. Two of the data channels in each record are reserved for an electronic check of the data logger. One data channel is programmed to read 0000 ± 0005 and the other to read 1600 ± 0010. If the value recorded in either data channel is not within the prescribed limits the recorded data values for all of the sensors is of questionable validity.

The second validity check, performed once each day, is designed to test the electronics of each sensor. This also is a two point check in that each sensor transmits a signal representative of 10 and 70 percent of scale. For the first 5-minute period the signal corresponding to 10 percent of scale is transmitted from the sensor to the data logger and then to the magnetic tape. Similarly for the next 5-minute period the signal for 70 percent of scale is written on the magnetic tape. Small tolerances are permitted for both levels on the scale. Should the value recorded on tape for a particular sensor fall outside of the acceptable range, all data for that sensor (since the prior sensor check) is of questionable value.

For a system involving the use of telemetry it is also necessary to include a validity check for data transmission.

6.3 Data Validation

Data validation is the final step in handling raw measurement data from air quality monitoring equipment or emission source testing. Data validation involves a critical review of a body of data in order to locate spurious values. It may involve only a cursory scan to detect extreme values or a detailed evaluation requiring the use of a computer. In either situation, when a spurious value is located, it is not immediately rejected. Each questionable value must be checked for validity.

6.3.1 Data Validation for Manual Techniques

Both the analyst and the laboratory supervisor should inspect intermittent air quality monitoring data and emission source testing data. At regular intervals, daily or weekly, results should be scanned for questionable values. This type of validation is most sensitive to extreme values, i.e. either unusually high or low concentrations.

The criteria for determining an extreme value are derived from prior data obtained at the particular sampling site (or a similar site if no previous data is available for a site). The data used to determine extremes may be the minimum and maximum concentrations for all prior data from a site. The decision criteria might also be based on minimum and maximum for each season, each month, or each day.

The time spent checking data that has been manually reduced by technicians depends on the time available and on the demonstrated abilities of the technicians to follow instructions. No agencies appear at this time to be using a specific formula for determining how much data should be checked for validity in a manual data reduction system. One air pollution control agency approached the problem in the following manner:

- A senior technician or supervisor was assigned to check approximately 10% of the data interpreted by each of four or five technicians. The 10% figure was arbitrary based on time availability and experience in finding errors.
- Data was checked for obvious trends or unusual values indicating possible reader bias.
- No statistical formula was applied to determine the significance of differences between readings interpreted by the technician and readings interpreted by the senior technician or supervisor. If the two values differed by more than two digits in the last significant figure, the data was judged unacceptable.
- Each analyst's technique of data interpretation was checked against written procedures describing the use of graphic aids to determine if those graphic aids had been properly used. The most significant errors originated from the technician deviating from the written procedures -- not from random error.

6.7.2 Data Validation for Computerized Techniques

A computer can be used not only to store and retrieve data but also for data validation. This will require the development of a specialized computer program. The system for checking extreme values in manual techniques also applies here. The criteria for extreme values can be refined to individual hours during the day. With this procedure an hourly average concentration for carbon monoxide of 15 ppm may not be considered as an extreme value for 8:00 A.M. but could be tagged as questionable if it appeared at 2:00 A.M.

Another indication of possible spurious data is a large difference in concentration for two successive time intervals. The difference in concentration, which might be considered excessive, may vary from one pollutant to another and quite possibly may vary from one sampling location to another for the same pollutant. Ideally this difference in concentration is determined through a statistical analysis of historical data. For example, it may be determined that a difference of 0.05 ppm in the SO_2 concentration for successive hourly averages occurs rarely (less than 5 percent of the time). But at the same station the hourly average CO concentration may change by as much as 10 ppm. The criteria for what constitutes an excessive change may also be linked to time of day.

The extent of the decision elements to be used in data validation can not be defined for the general case. Rather, the validation criteria should be tailored along the lines suggested above for varying types of air monitoring networks.

6.4 The Statistical Approach to Data Validation

6.4.1 Maintaining Data Quality in Manual Data Reduction Systems

Often the output from a continuous air monitoring device is an analog trace on a strip chart. Usually the strip charts are cut at weekly intervals and are sent to the data handling staff for interpretation. A technician may estimate by inspection the hourly average pollutant concentrations and convert the analog percent of scale to engineering units, e.g. ppm. He may also read daily maximum five minute or ten minute concentrations from the chart.

Reading strip charts is a tedious job subject to varying degrees of error. A procedure for maintaining a desirable quality for data manually reduced from strip charts is important. One procedure for checking the validity of the data reduced by a technician is to have another technician or the supervisor check the data. Because the values have been taken from the strip chart by visual inspection, some difference in the values derived by two individuals can be expected. When the difference exceeds a nominal amount and the initial reading has been determined to be incorrect, an error should be noted. If the number of errors exceeds a predetermined number, all data for the strip chart are rejected and the chart is read again by a technican other than the one who initially read the chart. The question of how many values to check can be answered by applying acceptance sampling techniques.

6.4.2 Acceptance Sampling Applications

Acceptance sampling can be applied to data validation to determine the number of data bits (individual values on a strip chart) that need to be checked to determine with a given probability that all the data bits are acceptable. The supervisor wants to know, without checking every data value, if a defined error level has been exceeded. From each strip chart with N data values, the supervisor can randomly inspect n data values. If the number of erroneous values is less than or equal to C, the rejection criteria, the values for the strip chart are accepted. If the number of errors is greater than C the values for the strip chart are rejected, and another technician is asked to read the chart.

The following discussion is meant only to explain how acceptance sampling can be applied. The procedure is relatively complex, and several types of acceptance sampling can apply. A procedure for any specific application should be developed by a competent individual who understands the statistical derivation of acceptance sampling.

Values of n (the number of data values to be checked) and C (the maximum number of errors that is acceptable) are selected to insure a high probability of acceptance of all the strip chart values if the error rate is P_1 or less. A low probability of acceptance is insured if the error rate is P_2 or greater. The probability of acceptance of all the strip chart values is $1-\alpha$ for an error rate of P_1 and β for an error rate of P_2. Typical values of α are 0.01, 0.05, and 0.10, and typical values of β are 0.05, 0.10, and 0.20. The error rate is the percent of erroneous values.

The probability levels α and β are subjectively chosen. To determine the probabilities to use, the risk of accepting bad data or of rejecting good data must be considered. If the risk is small the value for the α (the acceptance probability) and β (the rejection probability) may be set at 0.10 and 0.20 respectively. Decreasing the values of α and β increases the size of the sample required to be checked.

Another problem is determining values for P_1 and P_2 (the acceptable and the non-acceptable error rates). The acceptable error rate could be ten percent. If the number of erroneous values exceeds ten percent of all values checked, then the data for the entire strip chart could theoretically be rejected. From a practical standpoint, however, if the error rate is eleven percent, the strip chart may still be acceptable. The P_1 value represents the error rate that the supervisor is trying to maintain. The P_2 value represents the maximum error rate that can be tolerated. As the difference between the acceptable error rate and the non-acceptable error rate increases for small sample sizes, e.g. ten or less, the acceptance and rejection probabilities change significantly.

A technique that can be applied to determine the effect of varying n (the number of individual values checked) and C (the maximum number of erroneous values allowed) is that use of an operating characteristic (OC) curve. The OC curve (Figure 6.1) gives the probability of acceptance for various error rates. For the following example values of P between 0.02 and 0.20 are used.

Consider that the choices of sample size, n, are 10, 25, and 50. Consider the rejection criterion to be 2, i.e., if more than 2 errors occur, the strip chart is rejected. The next step is to compute the probability of 2 or fewer errors for all P values from 0.02 to 0.20.

The probabilities of 0, 1, or 2 errors for each sample size n and each error rate P can be evaluated from the binomial distribution. Since the values of P being considered are small, the Poisson distribution can be used to approximate the binomial distribution. The cumulative probability curves for the Poisson distribution can be approximated by use of a chart developed by Dodge and Romig.[26]

The OC curves for the values of n and C are shown in Figure 6.1. When n = 50 the probability of acceptance, if

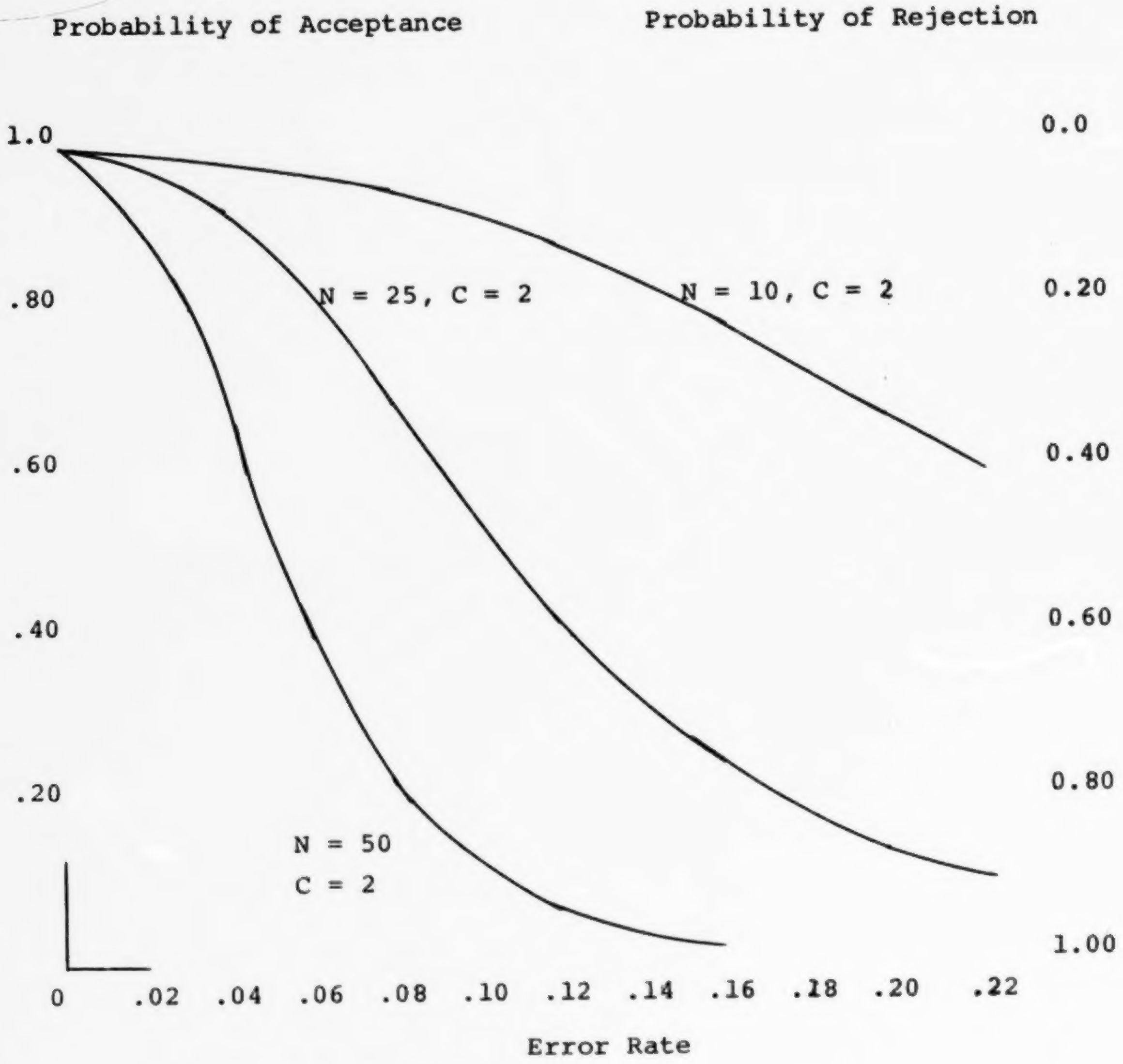


Figure 6.1 OC Curve

the error rate is P = 0.04, is approximately 0.68. But for the same sample size of 50, if the error rate is P = 0.02, the probability of acceptance if the error rate is P = 0.10 is approximately 0.12. If the sample size is n = 10 (and the acceptance criterion remains at C = 2) the probability of acceptance if P = 0.04 is approximately 0.99, and if P = 0.10 it is still approximately 0.92. So when the sample size decreases from 50 to 10 the test cannot discriminate well between error rates of 0.04 and 0.10.

It is apparent that establishing an acceptance plan for maintaining a defined quality of data is difficult. Various types of sampling plans are available. A quality control expert should be consulted before an acceptance sampling plan is adopted.

6.4.3 Sequential Analysis

6.4.3.1 Test Procedure - The typical approach used in performing a statistical test of hypothesis requires the collection of a sample of a fixed size. A statistic is then computed from the sample data and compared with some critical values for that statistic. A decision is then made to accept the hypothesis (H_o) or to accept some alternative hypothesis (H_1). With such a procedure it is necessary to collect the specified sample of observations regardless of the results that may be obtained from the first few observations.

A procedure called sequential analysis requires that a decision be made after each observation is made. The possible decisions to be made are;

1. Accept H_o.
2. Accept H_1.
3. Continue the sampling process.

This procedure has the advantage that, on the average, fewer observations are required to reach a decision than would be the case with a fixed sample size.

Sequential analysis is readily adaptable to acceptance sampling related to checking the error rate of an analyst responsible for reducing data from strip charts. Suppose that a random sample of data values read by one analyst is checked for validity by another (and probably more experienced) analyst. Each time the difference between two such readings exceeds some nominal value an error is said to have occurred in the original value. Suppose further that it is desired to reject a set of data only 5 percent of the time if the error rate of the analyst is less than 0.05 and accept the set of data only 10 percent of the time if the error rate is greater than 0.15.

$H_o : P = P_o \leq 0.05$

$H_1 : P = P_1 \geq 0.15$

$\alpha = 0.05$

$\beta = 0.10$

On the basis of the above information it is possible to construct the graph shown in Figure 6.2. The parallel lines define the critical regions for the three possible decisions, one of which must be made after each observation. The actual observational data is plotted on the graph as a step function (i.e. a line is drawn one unit to the right if a data value is determined to be valid and one unit up if the value is declared to be incorrect). The sampling process is stopped when the step function crosses either parallel line.

Suppose the following results are obtained when data values read by an analyst are checked for validity:

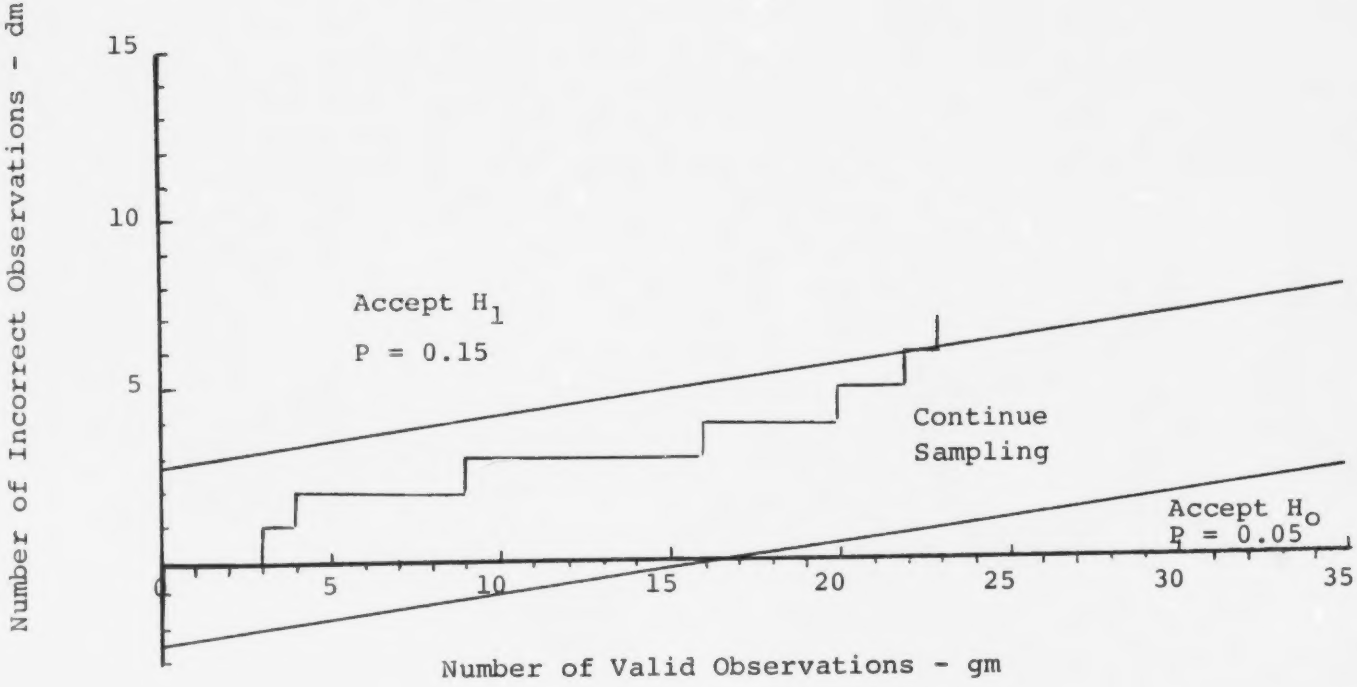


Figure 6.2 Sequential Test for the Error Rate of a Data Analyst

Observation	Result
1	g
2	g
3	g
4	b
5	g
6	b
7	g
8	g
9	g
10	g
11	g
12	b
13	g
14	g
15	g
16	g
17	g
18	g
19	g
20	b
21	g
22	g
23	g
24	g
25	b
26	g
27	g
28	b
29	g
30	b
31	g
32	g
33	g
34	b
35	g

The results can be plotted on Figure 6.2 by drawing a line one unit to the right if the data value is good (g) and one unit up if the data value is bad (b). After only a few observations it appears that the final outcome will be to reject the hypothesis that the analyst true error rate is equal to or less than 0.05. Indeed after the 30th observation (i.e. $g_m + d_m = 30$, where $g_m = 23$ and $d_m = 7$) the sampling process would be halted and the decision would be to accept H_1 (i.e. reject the hypothesis that the error rate is equal to or less than 0.05) indicating that the error rate of the analysis is not acceptable.

The equations of the parallel lines shown in Figure 6.2 are:

$$1.099\ d_m - 0.111\ g_m = 2.890 \quad (1)$$

$$1.099\ d_m - 0.111\ g_m = -2.255 \quad (2)$$

where d_m = number of errors out of m observations

g_m = number of valid values out of m observations

The general form of equations (1) and (2) is given by

$$d_m \ln \frac{P_1}{P_o} + g_m \ln \frac{1-P_1}{1-P_o} = \ln \frac{1-\beta}{\alpha} \quad (3)$$

and $$d_m \ln \frac{P_1}{P_o} + g_m \ln \frac{1-P_1}{1-P_o} = \ln \frac{\beta}{1-\alpha} \quad (4)$$

where P_o = 0.05 = acceptable error rate

P_1 = 0.15 = excessive error rate

α = 0.05 = probability of rejecting the set of data when the true error rate is ≤ 0.05

β = 0.10 = probability of accepting the set of data when the true error rate is ≥ 0.15

ln = natural logarithm of the term following

Substituting the values shown above in equations (3) and (4) yields;

$$d_m \ln \frac{0.15}{0.05} + g_m \ln \frac{1-0.15}{1-0.05} = \ln \frac{1-0.10}{0.05} \tag{6}$$

$$d_m \ln \frac{0.15}{0.05} + g_m \ln \frac{1-0.15}{1-0.05} = \ln \frac{0.10}{1-0.05} \tag{7}$$

The method of sequential analysis is based upon the computation of the sequential probability ratio P_{1m}/P_{om}. The denominator of this ratio, P_{om} is the probability that the m observations would occur if hypothesis H_o were true. Similarly P_{1m} is the probability that the m observations would occur if hypothesis H_1 were true. The test procedure followed is as follows:

1. if $\frac{P_{1m}}{P_{om}} \leq \frac{\beta}{1-\alpha}$, except H_o
2. If $\frac{P_{1m}}{P_{om}} \geq \frac{1-\beta}{\alpha}$, except H_1
3. If $\frac{\beta}{1-\alpha} < \frac{P_{1m}}{P_{om}} < \frac{1-\beta}{\alpha}$, take another observation.

If the error rate of the analyst is P_1, the probability of getting exactly d_m errors and g_m valid data values out of a set of m observations is

$$P_{1m} = P_1^{d_m} (1-P_1)^{g_m} \tag{8}$$

On the other hand if the error rate of the analyst is P_o

$$P_{om} = P_o^{d_m} (1-P_o)^{g_m} \tag{9}$$

The sequential probability ratio is

$$\frac{P_{1m}}{P_{om}} = \left(\frac{P_1}{P_o} \right)^{d_m} \left(\frac{1-P_1}{1-P_o} \right)^{g_m} \tag{10}$$

and the decision to accept H_o shown above becomes

$$\left(\frac{P_1}{P_o} \right)^{d_m} \left(\frac{1-P_1}{1-P_o} \right)^{g_m} \leq \frac{\beta}{1-\alpha} \tag{11}$$

Taking the natural logarithm of (11) yields

$$d_m \ln \frac{P_1}{P_o} + g_m \ln \frac{1-P_1}{1-P_o} \leq \ln \frac{\beta}{1-\alpha} \tag{12}$$

from which equation (4) is obtained by using the equality (i.e. the critical value). Equation (3) follows in a similar manner.

6.4.3.2 Operating Characteristic - The operating characteristic (OC) function is the function which defines the probability of acceptance when the error rate for the data analyst is P. For the example discussed above, four points on the OC curve are known;

Error Rate	Probability of Acceptance
(P)	(OC Function)
0	1
0.05	$1-\alpha = 0.95$
0.15	$\beta = 0.10$
1	0

An additional point between P_o and P_1 can be plotted for the proportion

$$P' = \frac{\ln \frac{1-P_1}{1-P_o}}{\ln \frac{1-P_1}{1-P_o} - \ln \frac{P_1}{P_o}}$$

and the corresponding probability of accepting P' as

$$Pr(P') = \frac{\ln \frac{1-\beta}{\alpha}}{\ln \frac{1-\beta}{\alpha} - \ln \frac{\beta}{1-\alpha}}$$

Substituting P_o, P_1, α and β for the example yields,

$$P' = \frac{\ln \frac{1-0.15}{1-0.05}}{\ln \frac{1-0.15}{1-0.05} - \ln \frac{0.15}{0.05}}$$

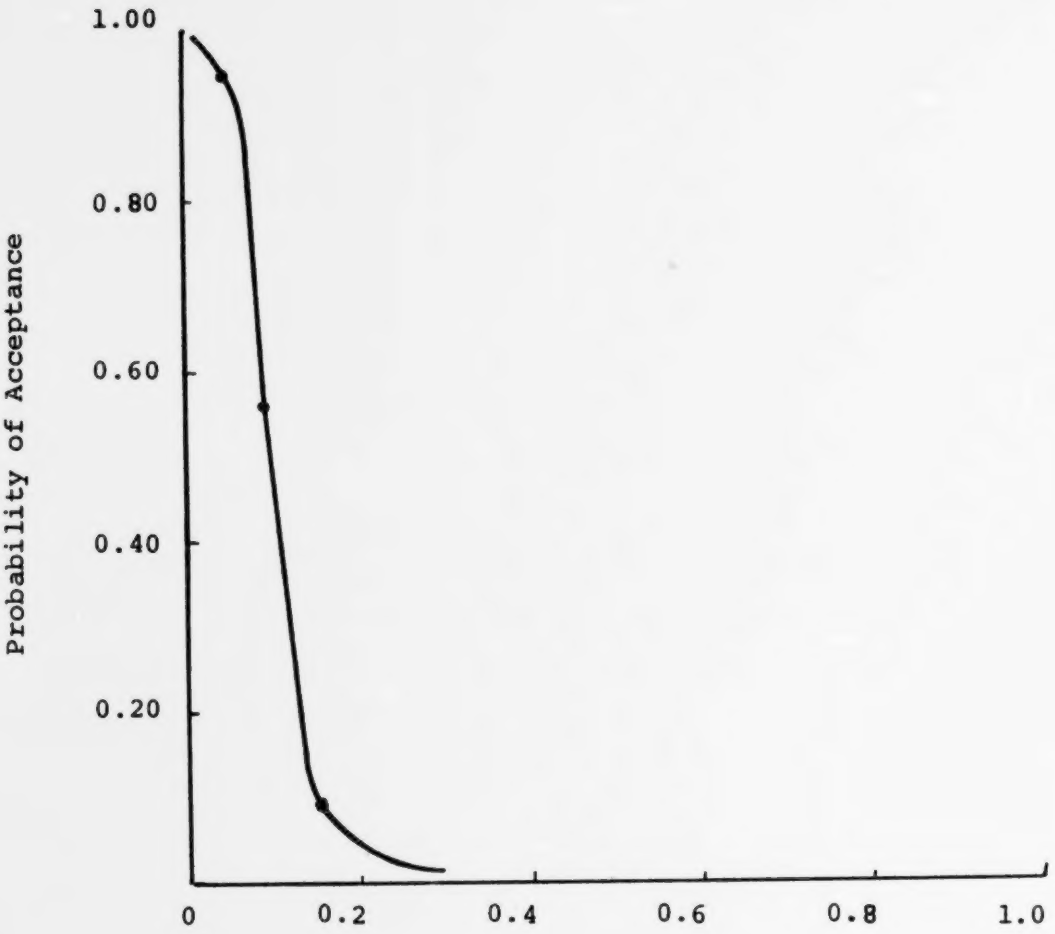
$$= 0.09$$

$$Pr(P') = \frac{\ln \frac{1-0.10}{0.05}}{\ln \frac{1-0.10}{0.05} - \ln \frac{0.10}{1-0.05}}$$

$$= 0.56$$

The OC curve for the example problem is presented in Figure 6.3. As can be seen if the actual error rate of the analyst is equal to or greater than 0.15 the probability of acceptance with this test procedure is small (<0.10). If, however the actual error rate of the analyst is about 0.10 the probability is about 0.5 that this test procedure will accept the set of data as having an acceptable error rate.

6.4.3.3 Average Sample Number (ASN) - It is obvious from Figure 6.2, that the sampling process to determine if the analyst is maintaining an acceptable error rate will terminate after a few observations if the error rate is much greater than P_1 or much smaller than P_o. On the other hand if the error rate is near or between P_1 and P_o it may



Error Rate - P

Figure 6.3 Operating Characteristic Curve

be necessary to check a large number of data values to ascertain whether or not the analyst is performing at a satisfactory level. Based on the example, if all of the data values that are checked are incorrect, the checking process will terminate after only 3 observations. Likewise if all values are valid the checking process will be stopped after 16 observations.

The average sample number (ASN) for the example problem for $P_o = 0.05$ is given by

$$\text{ASN} = \frac{(1-\alpha)\ \ln \frac{\beta}{1-\alpha} + \alpha\ \ln \frac{1-\beta}{\alpha}}{P_o\ \ln \frac{P_1}{P_o} + (1-P_o)\ \ln \frac{1-P_1}{1-P_o}}$$

$$= 40$$

Similarily for $P_1 = 0.15$ the ASN is given by

$$\text{ASN} = \frac{\beta\ \ln \frac{\beta}{1-\alpha} + (1-\beta)\ \ln \frac{1-\beta}{\alpha}}{P_1\ \ln \frac{P_1}{P_o} + (1-P_1)\ \ln \frac{1-P_1}{1-P_0}}$$

$$= 33$$

6.4.3.4 Observations in Groups - There may be situations when it is more efficient (from the standpoint of the collection of a sample of observations) to make several observations at a time and then record the results in a manner similar to that for the example problem above. It can be shown mathematicall that the ASN will be increased by an amount equal to the number of observations in each group. Thus the ASN's reported for P_o and P_1, above would be increased by 5 to 45 and 38 respectively.

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APPENDIX A

STATISTICAL FORMULAE AND DEFINITIONS

ARITHMETIC MEAN

$$\overline{X} = \frac{\sum_{1}^{n} X_i}{N}$$

$\overline{X}$ = mean value

X_i = individual value in the sample

N = number of values in the sample

RANGE

$$R = X_{max} - X_{min}$$

X_{max} = maximum value in the sample

X_{min} = minimum value in the sample

STANDARD DEVIATION

$$S = \sqrt{\frac{\Sigma (X_i - \overline{X})^2}{N - 1}}$$

X = individual value in the sample

$\overline{X}$ = average of all values in the sample

N = number of values in the sample

COEFFICIENT OF VARIATION

(also referred to as relative st deviation)

$$CV = \frac{S}{\overline{X}} (100)$$

S = standard deviation

$\overline{X}$ = mean value

CONTROL LIMITS FOR CONTROL CHARTS

RANGE CHART(27)

Upper Control Limit = UCL = $D_4\bar{R}$

$\bar{R}$ = average range for a set of replicates

D_4 = adjustment factor

$D_4 = 1 + 3\,\sigma'_w/d_2$

σ'_w = standard deviation of the relative range

d_2 = an adjustment factor used to estimate the standard deviation of a universe

Lower Control Limit = LCL = $D_3\bar{R}$

$\bar{R}$ = average range for a set of replicates

D_3 = adjustment factor

$D_3 = 1 - 3\,\sigma\, w/d_2$

COEFFICIENT OF VARIATION CHART(28)

Upper Control Limit = UCL = $B_4\,\overline{CV}$

$\overline{CV}$ = average coefficient of variation for a set of replicates

B_4 = adjustment factor

$$B_4 = 1 + \frac{K}{c_2}$$

$$K = 3\sqrt{\frac{N-1}{N} - c_2^2}$$

N = number of values in a sample

c_2 = an adjustment factor used to estimate the standard deviation of a universe

Lower Control Limit = $LCL = B_3\overline{CV}$

$\overline{CV}$ = average coefficient of variation for a set of replicates

$$B_3 = 1 - \frac{K}{c_2}$$

$$K = 3\sqrt{\frac{n-1}{n} - c_2^2}$$

N = number of values in a sample

c_2 = an adjustment factor used to estimate the standard deviation of a universe

CONTROL CHART FOR AVERAGES(29)

Upper control limit = $UCL = \bar{x} + A_2\bar{R}$

Lower control limit = $LCL = \bar{x} - A_2\bar{R}$

$$A_2 = \frac{3}{\sqrt{N}\, d_2}$$

N = number of values in a sample

d_2= an adjustment factor used to estimate the standard deviation of a universe.

APPENDIX B

TABLES OF FACTORS FOR CONSTRUCTING CONTROL CHARTS*

TABLE BI

FACTORS FOR CONSTRUCTING CONTROL CHARTS FOR AVERAGES

Observations in Sample, n	Factors for Control Limits A_2
2	1.880
3	1.023
4	0.729
5	0.577
6	0.483
7	0.419
8	0.373
9	0.337
10	0.308
11	0.285
12	0.266
13	0.249
14	0.235
15	0.223
16	0.212
17	0.203
18	0.194
19	0.187
20	0.180
21	0.173
22	0.167
23	0.162
24	0.157
25	0.153

*The factors in these tables are for the 99% confidence interval.

TABLE BII

FACTORS FOR CONSTRUCTING CONTROL CHARTS FOR RANGE

Number of Observations in Sample, n	Factors for Control Limits	
	D_3	D_4
2	0	3.267
3	0	2.575
4	0	2.282
5	0	2.115
6	0	2.004
7	0.076	1.924
8	0.136	1.864
9	0.184	1.816
10	0.223	1.777
11	0.256	1.744
12	0.284	1.716
13	0.308	1.692
14	0.329	1.671
15	0.348	1.652
16	0.364	1.636
17	0.379	1.621
18	0.392	1.608
19	0.404	1.596
20	0.414	1.586
21	0.425	1.575
22	0.434	1.566
23	0.443	1.557
24	0.452	1.548
25	0.459	1.541

TABLE BIII

FACTORS FOR CONSTRUCTING CONTROL CHARTS FOR COEFFICIENT OF VARIATION

Number of Observations in Sample, n	Factors for Control Limits	
	B_3	B_4
2	0	3.267
3	0	2.568
4	0	2.266
5	0	2.089
6	0.030	1.970
7	0.118	1.882
8	0.185	1.815
9	0.239	1.761
10	0.284	1.716
11	0.321	1.679
12	0.354	1.646
13	0.382	1.618
14	0.406	1.594
15	0.428	1.572
16	0.448	1.552
17	0.466	1.534
18	0.482	1.518
19	0.497	1.503
20	0.510	1.490
21	0.523	1.477
22	0.534	1.466
23	0.545	1.455
24	0.555	1.445
25	0.565	1.435

TABLE BIV

THE t DISTRIBUTION (TWO-TAILED TESTS)

Degrees of Freedom	Probability of a Larger Value, Sign Ignored 0.050	0.010
1	12.707	63.657
2	4.303	9.925
3	3.182	5.841
4	2.776	4.604
5	2.571	4.032
6	2.447	3.707
7	2.365	3.499
8	2.306	3.355
9	2.262	3.250
10	2.228	3.169
11	2.201	3.106
12	2.179	3.055
13	2.160	3.012
14	2.145	2.977
15	2.131	2.947
16	2.120	2.921
17	2.110	2.898
18	2.101	2.878
19	2.093	2.861
20	2.086	2.845

APPENDIX C

CALIBRATION CURVES FROM REGRESSION ANALYSIS BY THE METHOD OF LEAST SQUARES

E.1 Constructing the Calibration Curve

The calibration curve presented in Figure C-1 shows the relationship between the concentration of sulfur dioxide in the sample and absorbance (i.e. the instrument response). The calibration curve was determined on the basis of a least squares regression analysis in which the relationship between concentration (X) and absorbance (Y) is assumed to be of the form;

$$Y = a + bX$$

where a = intercept (i.e. the point at which the line crosses the Y axis)

b = slope (i.e. the change in absorbance per unit change in concentration)

Equations for determining a and b are:

$$b = \frac{N\sum_{i=1}^{N} X_iY_i - \sum_{i=1}^{N} X_i \sum_{i=1}^{N} Y_i}{N\sum^{N} X_i^2 - (\sum^{N} X_i)^2}$$

$$a = Y - bX$$

$$a = \frac{\sum_{i=1}^{N} Y_i}{N} \quad \frac{b\sum_{i=1}^{N} X_i}{N}$$

where N = 12 (the number of samples analyzed) as shown in Table C-1.

TABLE C-1

CALIBRATION DATA FOR SO_2 DETERMINATION

X	Y	X^2	Y^2	XY
.20	.095	.04	.009025	.0190
.20	.080	.04	.0064	.0160
.20	.123	.04	.015129	.0246
.60	.305	.36	.093025	.1830
.60	.329	.36	.108241	.1974
.60	.355	.36	.126025	.2130
1.00	.559	1.00	.312481	.559
1.00	.560	1.00	.313600	.560
1.00	.590	1.00	.348100	.590
1.40	.780	1.96	.6084	1.092
1.40	.810	1.96	.6561	1.1340
1.40	.790	1.96	.6241	1.106

$\Sigma X = 9.6$ $\quad \Sigma Y = 5.376$ $\quad \Sigma XY = 5.694$

$\bar{X} = .8$ $\quad \bar{Y} = .448$

$\Sigma X^2 = 10.08$ $\quad \Sigma Y^2 = 3.220626$

Substituting the appropriate summation from Table C-1:

$$b = \frac{12(5.694) - (9.6)(5.376)}{12(10.08) - (9.6)^2}$$

$$b = 0.5805$$

$$a = \frac{5.376}{12} - \frac{(0.5805)(9.6)}{12}$$

$$a = -0.0164$$

The equation for the calibration line is:

$$Y = -0.0164 + 0.5805X$$

To plot this straight line (Figure C-1) two points in the XY plane are necessary. One point is the Y intercept, that is when X = 0, Y = -0.0164. A second point can be selected for any other value of X, for example, X = 1.2. Then

$$Y = -0.0164 + 0.5805\ (1.2)$$

$$Y = 0.6802$$

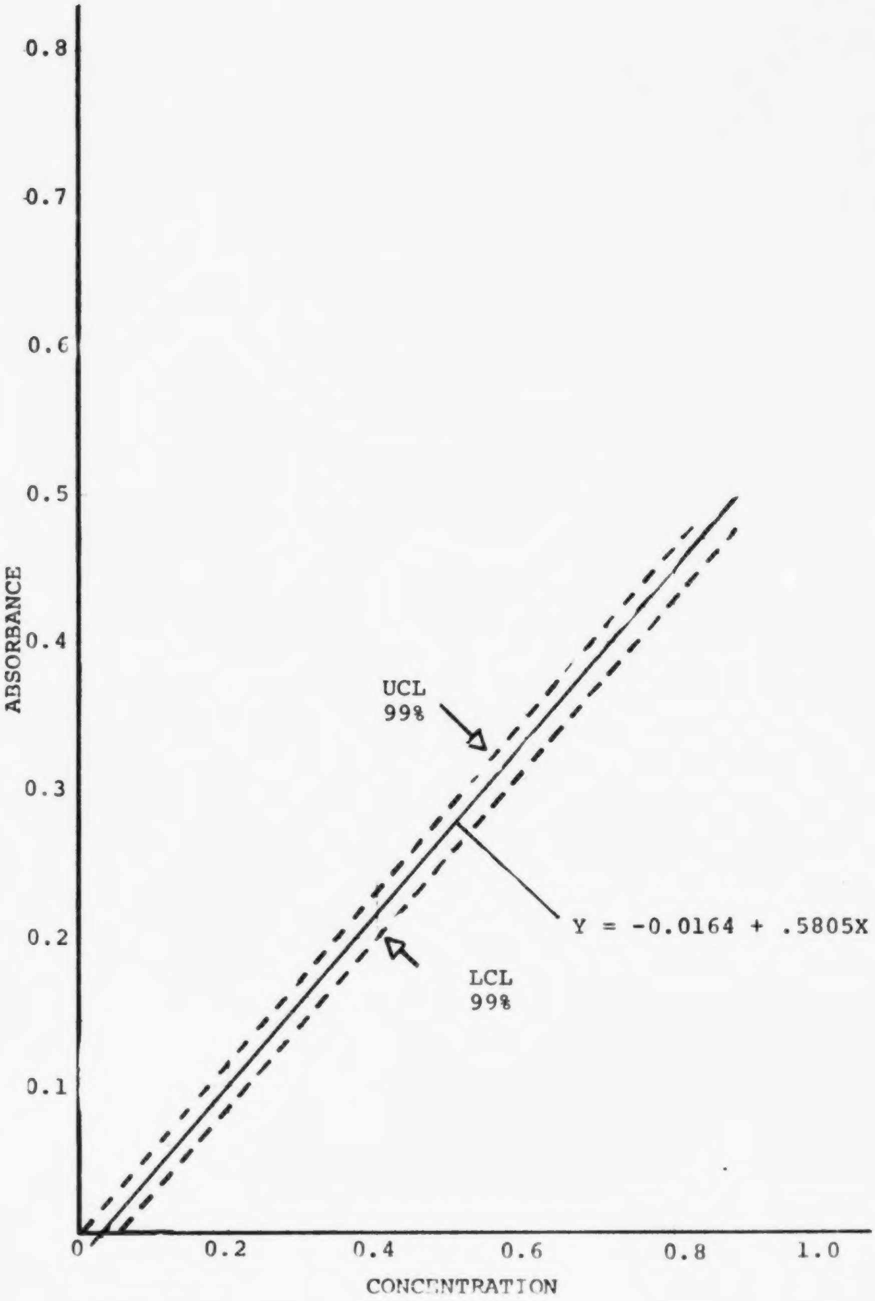

Figure C-1. Calibration Curve for SO_2 Determination